UNIVERSITY OF BIRMINGHAM

Brominated Flame Retardants in Indoor Environments with a Focus on Kitchens

By

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Abstract

Brominated flame retardants (BFRs) are a group of organic compounds added in flammable materials to retard fire ignition and have raised great concern due to their ubiquitous occurrence, persistency and toxicity. To investigate BFR contamination in kitchens and related human exposure, we collected paired kitchen-living room dust samples from 30 UK houses and 14 wipe samples of kitchen appliances for the analysis of BFRs, including PBDEs, HBCDDs and novel BFRs PBEB, EH-TBB, BTBPE, BEH-TEBP and DBDPE. Moreover, 96 plastic kitchen utensils were collected, screened for Br concentration by XRF spectrometer, with 30 utensils analysed for BFR concentrations. A simulated cooking experiment was conducted to evaluate BFR exposure via using contaminated utensils. Temporal and geographical differences in concentrations of BFRs in indoor dust samples were investigated via comparing BFR concentrations in UK samples in 2006-07 and 2015, and comparing 116 indoor house dust samples collected between 2014-15 from 6 countries (Finland, Greece, Spain, Jordan, US and Mexico) respectively. In dust samples, BDE-209 was found to be the most abundant BFR, followed by DBDPE, BEH-TEBP, HBCDDs, BDE-99 and BDE-47. Concentration of BDE-209 was found to decrease in the UK since 2006, and corresponding increase of its substitute DBDPE was observed. Higher concentrations were observed in UK living room dust than in kitchens for all BFR. Wipe samples indicated the presence of non-targeted FRs such as TBBPA in kitchen appliances, which may partly explain the lower target BFR concentrations in kitchens. US dust samples

showed the highest Penta-BDE concentrations, followed by Mexican dust. Jordanian dust samples contained the highest mean concentrations of Octa-BDE. With respect to Deca-BDE, concentrations were not significantly different between the studied countries. For NBFRs, US and Mexican samples were found to display a similar composition to that found in the FireMaster® 550 formulation (EH-TBB:BEH-TEBP=4:1). Higher Br and BFR concentrations were observed in old utensils (> 5 years) than in new ones, and BDE-209 was the most abundant BFR in the majority of utensils. Simulated cooking experiments revealed considerable BFR transfer from kitchen utensils to cooking oils. Estimated median exposure via cooking with BFR contaminated utensils was 60 ng/day for total BFRs, with BDE-209 accounted for 50 ng/day. In contrast, estimated exposure via dermal contact with BFR-containing kitchen utensils was less substantial. Our results implicate the exposure risk of BFRs in kitchen, change of BFR application pattern due to restriction of legacy BFRs, and various application pattern in different countries.

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List of Abbreviations

APCI	Atmospheric Pressure Chemical Ionisation
BEH-TEBP	Bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate
BFR	Brominated Flame Retardant
BTBPE	1,2-bis(2,4,6-tribromophenoxy)ethane
bw	body weight
DBDPE	Decabromodiphenyl ethane
dw	dry weight
ECNI	Electron Capture Negative Ionisation
EH-TBB	2-ethylhexyl-2,3,4,5-tetrabromobenzoate
EI	Election Ionisation
ESI	Electrospray Ionisation
FCA	Food Contact Article
FR	Flame Retardant
GC-MS	Gas Chromatography-Mass Spectrometry
GM	Geometric Mean
HBCDD	Hexabromocyclododecane
K_{ow}	n-octanol/water partition coefficient
K_{oa}	n-octanol/air partition coefficient
LC-MS	Liquid Chromatography-Mass Spectrometry

LPCL	Low POP Concentration Limit
lw	lipid weight
m/z	mass to charge ratio
NBFR	Novel Brominated Flame Retardant
OPFR	Organophosphorus Flame Retardant
PBDE	Polybrominated Diphenyl Ether
PBEB	Pentabromoethylbenzene
PCA	Principal Component Analysis
POP	Persistent Organic Pollutant
QA/QC	Quality Assurance/Quality Control
SRM	Standard Reference Material
TBBPA	Tetrabromobisphenol-A
UNEP	United Nations Environment Programme
US DHHS and DA	Uinted States Department of Health and Human Services and United States Department of Agriculture
US EPA	United States Environmental Protection Agency
WEEE	Waste Electrical and Electronic Equipment
WHO	World Health Organisation
ww	wet weight
XRF	X-Ray Fluorescence

List of Publications and Conference Presentations

Publications

Kuang, J., Abdallah, M.A.-E., Harrad, S., 2017. Brominated flame retardants in black plastic kitchen utensils: Concentrations and human exposure implications. Science of the Total Environment. (Accepted)

Cao, Z., Zhao, L., **Kuang, J.**, Chen, Q., Zhu, G., Zhang, K., Wang, S., Wu, P., Zhang, X., Wang, X., Harrad, S., Sun, J., 2017. Vehicles as outdoor BFR sources: Evidence from an investigation of BFR occurrence in road dust. Chemosphere 179, 29-36.

Kuang, J., Ma, Y., Harrad, S., 2016. Concentrations of "legacy" and novel brominated flame retardants in matched samples of UK kitchen and living room/bedroom dust. Chemosphere 149, 224-230.

Conferences

Kuang, J., Abdallah, M., Harrad, S., BFR contamination in UK kitchen utensils: Implications for human exposure via transfer to cooking oil and direct dermal contact, 8th International Symposium on Flame Retardants, 7-10 May, 2017, York, UK (Poster)

Kuang, J., Harrad, S., BFR contamination in UK kitchen utensils: Implications for human exposure, 5th UK and Ireland Exposure Science Meeting, 29 Mar, 2017, Birmingham, UK (Poster)

Kuang, J., Ma, Y., Harrad, S., Concentrations of "legacy" and novel brominated flame retardants in matched samples of UK kitchen and living room/bedroom dust, 36th International Symposium on Halogenated Persistent Organic Pollutants, 28 Aug-2 Sept, 2016, Firenze, Italy (Oral)

Kuang, J., Ma, Y., Carrizales, Y., Harrad, S., Concentrations of PBDEs, NBFRs and HBCDDs in living room dust from Finland, Spain, Greece, Jordan, United States and Mexico, 36th International Symposium on Halogenated Persistent Organic Pollutants, 28 Aug-2 Sept, 2016, Firenze, Italy (Poster)

Kuang, J., Harrad, S., Ma, Y., Mortimer, D., PBDEs and NBFRs in UK kitchen dust, 7th International Symposium on Flame Retardants, 21-24 Apr, 2015, Beijing, China (Poster)

Chapter 1 Introduction

1.1 Overview of BFRs

1.1.1 Definition and classification

Flame retardants (FRs) are a group of chemicals added to combustible materials such as building materials, upholstery, textiles, polymers, circuit boards and electronic device cases to retard and prevent fire ignition, with the intention of preventing fire deaths, or at least offering more time for people to escape. They are widely used to meet mandatory flame retardancy requirements. The application history of FRs can be traced back to 450 BC, when ancient Egyptians used alum to flame retard wood, and later, in about 200 BC, ancient Romans improved the formulation (Hindersin, 1990 cited by Alaee and Wenning, 2002). At the present time, more than 175 kinds of FRs have been developed, which can be categorized into 4 sub-groups according to their chemical structure: inorganic FRs, organophosphorus FRs, nitrogen-containing FRs and halogenated organic FRs (Birnbaum and Staskal, 2004). Inorganic FRs include metal hydroxides such as aluminium hydroxide and magnesium hydroxide, ammonium polyphosphate, and red phosphorus (Segev et al., 2009). Of nitrogen-containing FRs, the most important ones are melamine and its derivatives (Segev et al., 2009), while organophosphorus FRs (OPFRs), together with halogenated organic FRs, comprise the mainstream FRs used in the market (Iqbal et al., 2017).

To understand the action mechanism of FRs, a brief introduction of combustion process is necessary. When heated at a high enough temperature (ignition point), the combustible material will undergo pyrolysis and emit combustible gases. The combustible gases then mix with oxygen and trigger a radical chain reaction, generating visible flame (light) and heat. The generated heat can then decompose combustible material further, emitting more combustible gases to propagate the reaction (Figure 1.1). Interruption at any step of combustion can retard flame, such as 1) separate oxygen and combustible gases; 2) dilute oxygen-combustible gas mixture; 3) terminate radical chain reaction and 4) absorb heat and reduce temperature (Figure 1.2). For example, the dehydration of aluminum hydroxide is an endothermic reaction, resulting in diluting and lowering the temperature of the flame, thus retard the flame (Alaee et al., 2003).

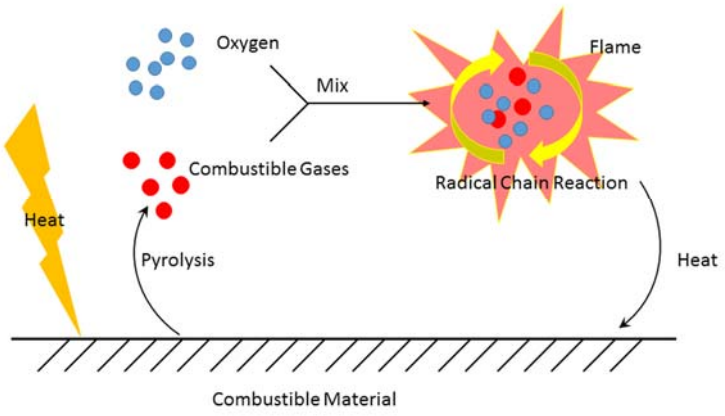


Figure 1.1: Process and mechanism of combustion

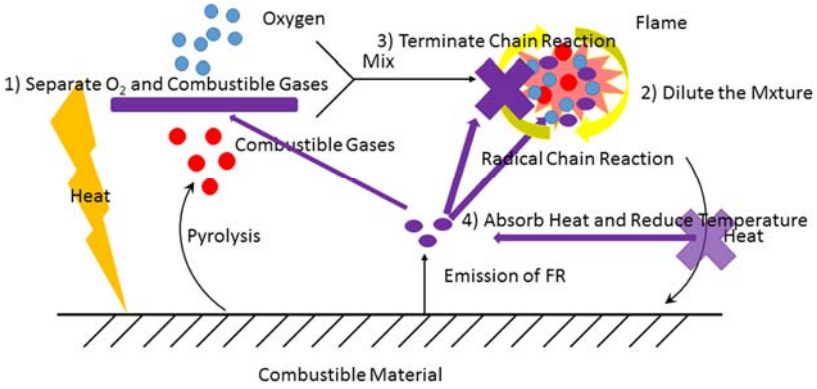


Figure 1.2: Mechanism of flame retardation

The mechanism of halogenated FRs is mainly terminating radical chain reaction. As shown by equation (1) – (4), hydroxyl radicals, oxygen radicals and hydrogen radicals are important radicals involving in chain reaction of combustion.

$$\bullet OH + CO \rightarrow CO_2 + H\bullet \quad (1)$$

$$\bullet OH + RCH_3 \rightarrow RCH_2\bullet + H_2O \quad (2)$$

$$RCH_2\bullet + O_2 \rightarrow RCHO + \bullet OH \quad (3)$$

$$H\bullet + O_2 \rightarrow \bullet OH + \bullet O\bullet \quad (4)$$

However, when heated, halogen atoms will be emitted from halogenated FRs in the form of radicals that act as radical scavengers, acting with hydroxyl radicals, oxygen radicals and hydrogen radicals and thus quenching the radical chain reaction of combustion (equation 5 – 9) (Abdallah, 2009; Chen et al., 2012; D'Silva et al., 2004).

$$RX \rightarrow R\bullet + X\bullet \quad (5)$$

$$X\bullet + RH \rightarrow HX + R\bullet \quad (6)$$

$$HX + \bullet OH \rightarrow H_2O + X\bullet \quad (7)$$

$$HX + \bullet H \rightarrow H_2 + X\bullet \quad (8)$$

$$HX + \bullet O\bullet \rightarrow \bullet OH + X\bullet \quad (9)$$

In the halogen family, fluorine is not practically used in flame retardant as the fluorine-carbon bond is too strong to release fluorine radical. On the contrary, iodine-carbon bond is too weak to stay stable before pyrolysis. For the remaining halogens, bromine radicals can be released at a more appropriate temperature (close to combustion temperature) and show a higher radical quenching efficiency than chlorine (Alaee et al., 2003; D'Silva et al., 2004). In addition to terminating radical chain reaction, halogenated FRs can release inert gases to dilute the concentration of oxygen and combustible gas, reduce the temperature, and thus retard combustion (Chen et al., 2012).

Considering the effectiveness, combined with their low cost, brominated FRs (BFRs) occupy the largest market (Birnbaum and Staskal, 2004). Today there are more than 75 kinds of BFRs (Alaee et al., 2003; Covaci et al., 2011). According to the structure of the carbon skeleton, BFRs can be categorized into aliphatic, cyclo-aliphatic and aromatic ones. Dibromoneopentyl glycol (DBNPG) and hexabromocyclododecane (HBCDD) are example for aliphatic and cyclo-aliphatic BFRs, respectively (Figure 1.3). Aromatic BFRs are more temperature resistant than aliphatic and cyclo-aliphatic ones (D'Silva et al., 2004), and have more family members (Figure 1.3), including polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol-A (TBBPA), bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP), decabromodiphenyl ethane (DBDPE).

According to the way in which they are incorporated into materials, BFRs can be categorized into additive BFRs, reactive BFRs and brominated monomers (Alaee et al., 2003). Additive BFRs like PBDEs, HBCDDs and DBDPE are only physically mixed with polymers, and thus prone to release during product use. In contrast, reactive BFRs, including tetrabromophthalic anhydride (TBPA), TBBPA and TBBPA derivatives are chemically bonded with polymers (D'Silva et al., 2004). Brominated monomers like brominated styrene and brominated butadiene are first converted into brominated polymers, than blended with normal polymers (Alaee et al., 2003).

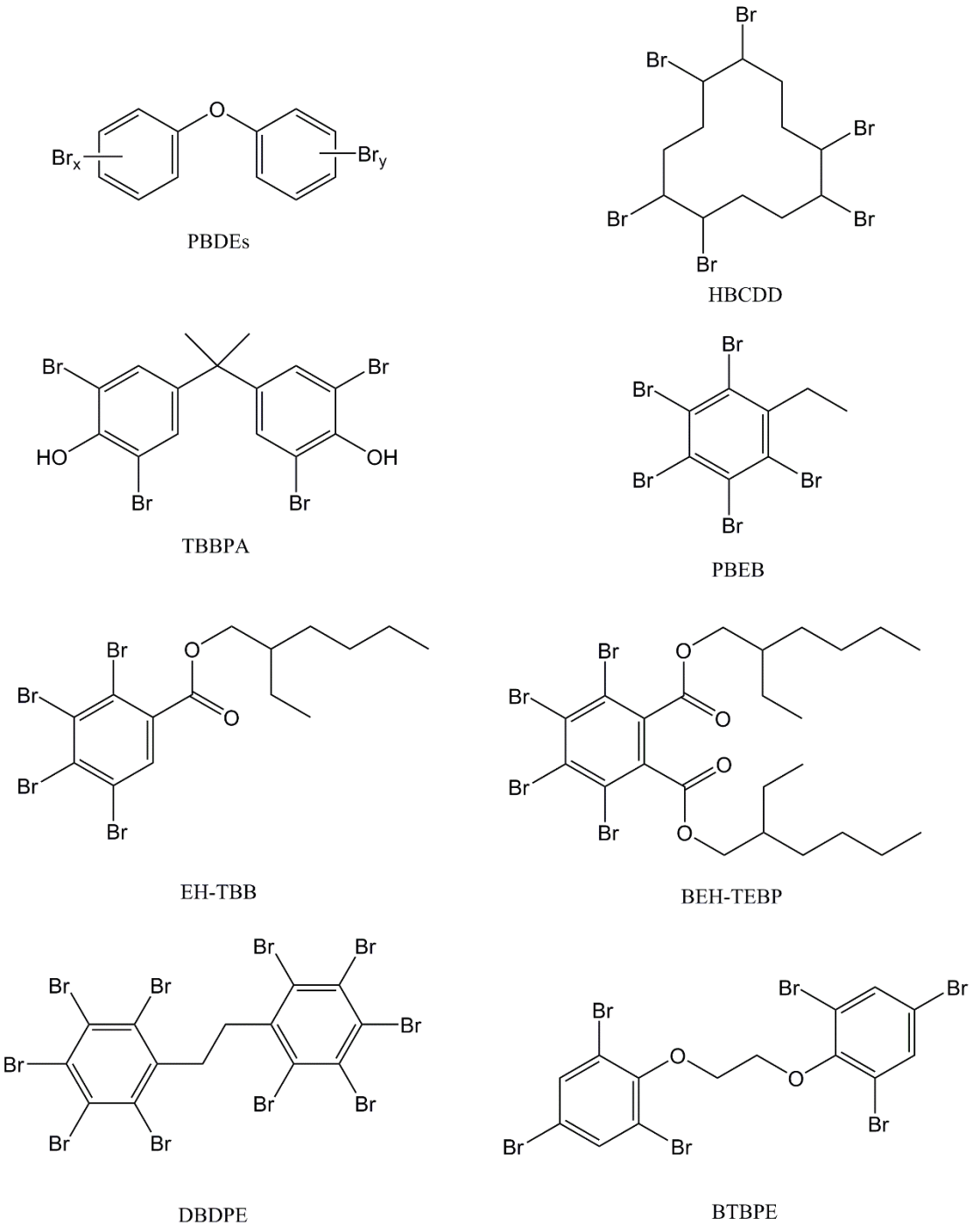


Figure 1.3: Structure of some important BFRs

Considering their application history, BFRs can also be divided into “traditional”/ “legacy” BFRs, and “novel”/“new” BFRs (NBFRs). Legacy BFRs mainly refer to PBDEs, HBCDDs and TBBPA, which have a longer application history. NBFRs are a group of substitutes for legacy BFRs. Besides DBDPE and BEH-TEBP mentioned

above, NBFRs also include pentabromoethylbenzene (PBEB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE).

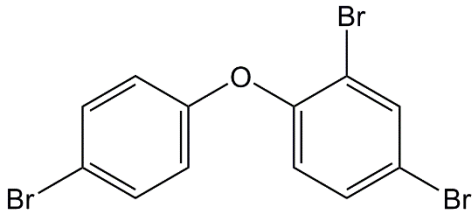
1.1.2 Usage and applications

1.1.2.1 PBDEs

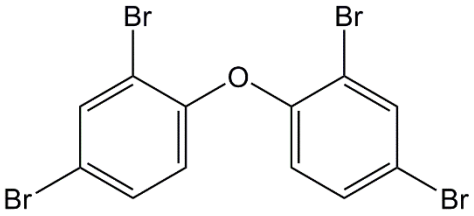
PBDEs have in total 209 congeners based on the different number and substitution positions of bromine (Figure 1.4) and the commercial used PBDEs are mixtures of congeners. There are 3 commercial PBDE formulations that were marketed, i.e. Penta-BDE, Octa-BDE and Deca-BDE (Table 1.1).

Table 1.1: PBDE homologue content (%) of the commercial mixtures Penta, Octa and Deca-BDE in 1997 and 2000 (Chen et al., 2012)

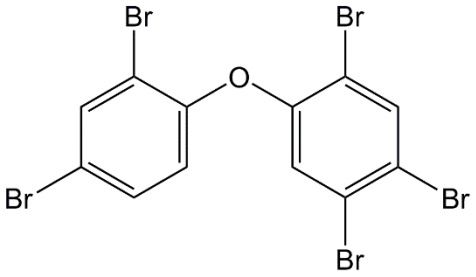
Homologue	PentaBDE		OctaBDE	DecaBDE
	1997	2000	1997	1997
tri-BDE	-	0.23	-	-
tetra-BDE	33.7	23.01	-	-
penta-BDE	54.6	55.1	-	-
hexa-BDE	11.7	8.58	5.5	-
hepta-BDE	-	-	42.3	-
octa-BDE	-	-	36.1	0.04
nona-BDE	-	-	13.9	2.5
deca-BDE	-	-	2.1	97.4



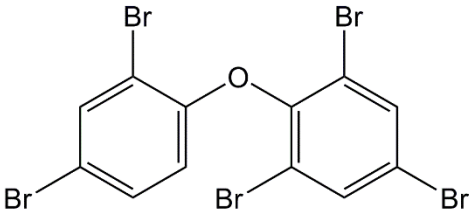
BDE-28



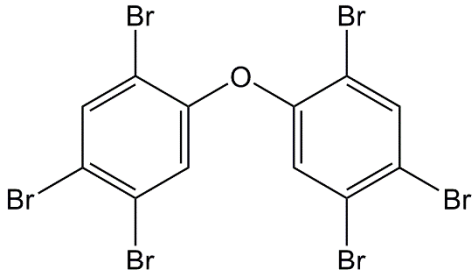
BDE-47



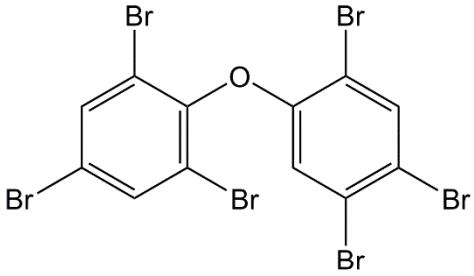
BDE-99



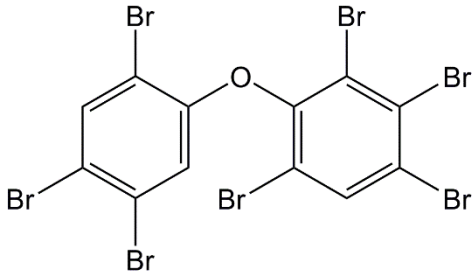
BDE-100



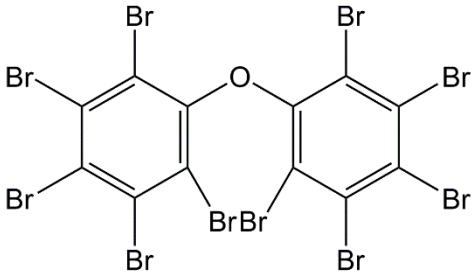
BDE-153



BDE-154



BDE-183



BDE-209

Figure 1.4: Structure of main BDE congeners

Penta-BDE is a viscous liquid containing 70 % bromine by weight comprising mainly tetra-BDE (BDE-47) and penta-BDE (BDE-99 and -100) (Table 1.1), with lesser contributions from hexa-BDE (BDE-153, 154) (Alaee et al., 2003). The main application of Penta-BDE is in rigid and flexible polyurethane foams and polyurethane elastomers, which are mostly used in upholstery and furnishings (D'Silva et al., 2004; Yogui and Sericano, 2009). The most widely known commercial Penta-BDE products are Bromkal 70-DE® produced by Great Lakes Chemicals (D'Silva et al., 2004), with almost all (97 %) Penta-BDE consumed by North America (Alaee et al., 2003). Octa-BDE is a white powder containing 79 % bromine by weight and the representative congener is BDE-183 (Alaee et al., 2003). Octa-BDE is mainly used in hard plastic such as acrylobutadienestyrene (ABS) and high-impact polystyrene (HIPS), which in turn is used in housing for electronic devices (D'Silva et al., 2004; Yogui and Sericano, 2009). Deca-BDE is a white powder containing 83 % bromine by weight (Alaee et al., 2003). Unlike Penta- and Octa-BDE, Deca-BDE mainly consists of one congener only (97-98 % BDE-209). Moreover, its applications are wider as it can be used in nearly all types of polymers including textiles, resins and plastics (Alaee et al., 2003; Yogui and Sericano, 2009). The wider application of Deca-BDE leads to a larger market demand, as estimated by BSEF, in 2001, worldwide market demand for Penta-, Octa- and Deca-BDE was 7,500, 3,790 and 56,100 tonnes, respectively (de Wit et al., 2010). More detailed applications of PBDEs are summarized in Table 1.2.

Table 1.2: Applications of PBDE commercial mixtures (D'Silva et al., 2004)

Resins and polymers	Deca-BDE	Octa-BDE	Penta-BDE
Acrylonitrile–butadiene–styrene		√	
Epoxy-resins	√		
Phenolic resins	√		√
Polyacrylonitrile	√		
Polyamide	√	√	
Polybutadiene terephthalate	√	√	
Polyethylene	√		
Polyethylene terephthalate	√		
Polypropylene	√		
Polystyrene (high impact)	√	√	
Polyvinyl chloride	√		√
Polyurethane			√
Polyesters	√		√
Rubber	√		√
Paints/lacquers	√		√
Textiles	√		√

1.1.2.2 HBCDDs

The IUPAC name of HBCDD is 1,2,5,6,9,10-hexabromocyclododecane, and it has 6 pairs of enantiomers and 4 meso forms (Heeb et al., 2005). In application, there are mainly 3 diastereoisomers, namely α-, β- and γ-HBCDD, accounting for 1-12 %, 10-13 % and 75-89 % in the commercial mixture, respectively. In addition, another 2 stereoisomers δ- and ε-HBCDD are also present in minor concentrations (Heeb et al., 2005). HBCDD is mainly used in extruded and high-impact polystyrene foams which are mainly used for building insulation and upholstery (Covaci et al., 2006). In 2001, the worldwide market demand for HBCDD was 16,700 tonnes.

1.1.2.3 NBFRs

With a similar structure to BDE-209, DBDPE is used as substitute for Deca-BDE under the commercial name of Saytex® 8010 (Albemarle Corp.) and Firemaster® 2100 (Chemtura Corp.) in HIPS, ABS, polypropylene (PP) and textiles (Covaci et al., 2011). BTBPE is used as a replacement for Octa-BDE under the commercial name FF-680 (Chemtura Corp.) added to ABS, HIPS, thermoplastics, thermoset resins, polycarbonate and coatings (WHO, 1997). EH-TBB and BEH-TEBP are used in a ratio of 4:1 in Firemaster® 550 (Chemtura Corp.) as replacement for Penta-BDE used in polyurethane foam (PUF) (Stapleton, 2008). Also, BEH-TEBP can be used in polyvinyl chloride (PVC), neoprene, wire and cable insulation, film and sheeting, carpet backing, coated fabrics, wall coverings and adhesives (Covaci et al., 2011). PBEB is mainly used in thermoset polyester resins like circuit boards, textiles, adhesives, wire and cable coatings, and polyurethane foam (Hoh et al., 2005; WHO, 1997). Compared with PBDEs and HBCDDs, the production information about NBFRs is scarce with large uncertainty. Harju et al. (2009) estimated the production volume of 21 NBFRs could be around 180,000 tonnes/year based on the assumption that production volumes have varied little over past years.

1.1.3 Physico-chemical properties

The main physico-chemical properties of some BFRs are summarized in Table 1.3, showing that most possess low water solubility, high K_{ow} and K_{oa}, and medium to low vapour pressures.

Table 1.3: Physico-chemical properties of some important BFRs (data collected from Al-Omran, 2016; Bergman et al., 2012; Covaci et al., 2011; Rauert, 2014; Tao, 2016; US EPA, 2010)

Compound	Formula	Molecular weight, Da	Water solubility, µg/L (25 °C)	Log K_{ow} (25 °C)	Log K_{oa} (25 °C)	Vapor pressure, Pa (25 °C)
BDE-28	$C_{12}H_7Br_3O$	407.1	70	5.94	9.5	2.19×10^{-3}
BDE-47	$C_{12}H_6Br_4O$	485.8	1-2	6.81	10.53	1.86×10^{-4}
BDE-99	$C_{12}H_5Br_5O$	564.8	9	7.32	11.31	1.76×10^{-5}
BDE-100	$C_{12}H_5Br_5O$	564.8	40	7.24	11.13	2.86×10^{-5}
BDE-153	$C_{12}H_4Br_6O$	643.6	1	7.9	11.82	2.09×10^{-6}
BDE-154	$C_{12}H_4Br_6O$	643.6	1	7.82	11.92	3.80×10^{-6}
BDE-183	$C_{12}H_3Br_7O$	722.4	2	8.27	11.96	4.68×10^{-7}
BDE-209	$C_{12}Br_{10}O$	959.2	<1	6.27	13.21	4.63×10^{-6}
PBEB	$C_8H_5Br_5$	500.7	350	6.40	9.9	3.2×10^{-4}
EH-TBB	$C_{15}H_{18}Br_4O_2$	549.9	11.4	7.73	12.34	3.71×10^{-7}
BTBPE	$C_{14}H_8Br_6O_2$	687.6	19.0	7.88	15.67	3.88×10^{-10}
BEH-TEBP	$C_{24}H_{34}Br_4O_4$	706.1	1.60	10.08	16.86	1.55×10^{-11}
DBDPE	$C_{14}H_4Br_{10}$	971.2	0.21	11.1	19.22	6.0×10^{-15}
α-HBCDD	$C_{12}H_{18}Br_6$	641.7	48.8	5.59	14.43	1.05×10^{-8}
β-HBCDD	$C_{12}H_{18}Br_6$	641.7	14.7	5.44	14.64	5.82×10^{-9}
γ-HBCDD	$C_{12}H_{18}Br_6$	641.7	2.1	5.53	14.17	8.39×10^{-11}

1.2 Occurrence of BFRs in environment

BFRs can migrate to the environment along the whole lifetime of products in which they are incorporated. Firstly, BFRs can enter the aquatic environment via wastewater from BFR manufacturing effluent (Iqbal et al., 2017). Moreover, during use of BFR-treated products, BFRs can migrate into air and dust through volatilization, weathering and absorption (Cao et al., 2013; Weschler and Nazaroff, 2008). Further, during the end of life phase, BFRs in products can migrate into the environment during waste disposal via leaching from landfills (Chen et al., 2012), contaminating soil and groundwater. As

shown above, BFRs possess high K_{ow} values and low water solubility, which means they are highly lipophilic. When entering the environment, they favour migrating to organic phases such as sediment, dust, and lipid of biota. Their semi-volatile vapour pressures determines they will partition between gas and solid phases, and undergo repeated vaporization-precipitation cycling, transporting far away from source sites (Dickhut et al., 2012; Scheringer, 2009; Zhu et al., 2013). Moreover, most of them are resistant to chemical and biological degradation, which renders BFRs environmentally persistent (Covaci et al., 2006; de Wit, 2002; Muir and Howard, 2006; Segev et al., 2009). Considering this alongside their large production volumes and long application history, BFRs are expected to display wide distribution in the environment.

1.2.1 Abiotic occurrence

1.2.1.1 BFRs in the indoor environment

Considering the large quantities of flame retarded goods and materials (upholstery, building insulation, electronic devices) that exist in a small, closed space, and also the large proportion of time people stay indoors; the indoor environment is of significant concern with respect to BFR contamination.

Watkins et al. (2013) measured concentrations of PBDE congeners in 31 office dust samples in Boston, US and found that BDE-209 showed the highest concentration, with a geometric mean concentration of 4,000 ng/g, and a range of 1,000 to 100,000 ng/g.

BDE-47 and BDE-99 showed lower concentrations, with geometric means of 600 and 900 ng/g, respectively. Geometric mean concentrations of other congeners lay between 10 to 100 ng/g.

Thuresson et al. (2012) studied concentrations of PBDEs and HBCDDs in dust and air of houses, apartments, day care centres, offices and cars in Stockholm, Sweden, concluding that day care centres and offices displayed the highest ΣPBDE concentrations in air, with median value of 4,000 and 14,000 pg/m^3 respectively. However, concentrations in dust displayed less variation between microenvironment categories, with median concentrations in all microenvironments ranging around 1,200 ng/g. HBCDDs were detected in most dust samples (median range 50-300 ng/g), but only in a few air samples (median range <1.6-2.0 pg/m^3).

Harrad et al. (2010) measured PBDE and HBCDD concentrations in UK primary school and day care centre classroom dust, finding median concentrations of BDE-209 and ΣHBCDDs to be 5,000 and 4,000 ng/g, respectively. Concentrations of other PBDEs were relatively low, ranging from not detected to several hundred ng/g. In another study of Harrad et al. (2008), concentrations of PBDEs, BTBPE and DBDPE were measured in dust from UK homes, offices and cars. Median concentrations of BDE-209 were 8,100, 6,200 and 10,000 ng/g in home, office and car dust respectively. Concentrations of other BFRs were fairly low compared to those of BDE-209, with median

concentrations ranging from not detected to several tens ng/g. Abdallah et al. (2008) investigated HBCDDs and TBBPA in dust and air from several UK microenvironments. Median concentrations for ΣHBCDDs in air from homes, offices, public microenvironments and outdoors were 180, 170, 900 and 37 pg/m^3, respectively. The corresponding data for TBBPA were 15, 11, 27 and 1 pg/m^3. Median concentrations in dust of ΣHBCDDs in homes, offices, cars and public microenvironments were 1,300, 760, 13,000 and 2,700 ng/g respectively. The corresponding data for TBBPA were 62, 36, 2 and 230 ng/g.

Bjorklund et al. (2012b) investigated PBDE concentrations in indoor air from different microenvironments in Stockholm, Sweden. The median concentrations of ΣPBDEs in apartments, offices and day care centres were 93, 3,700 and 660 pg/m^3, respectively. In all microenvironments, BDE-209 predominated, with median concentrations of 22, 1,900 and 340 pg/m^3 in apartments, offices and day care centres, respectively.

Extremely high BFR concentrations were observed in some specially flame retarded environments. Carignan et al. (2013) investigated FRs in US gym air and dust, reporting μg/g median concentrations for target BFRs in dust, and ng/m^3 concentrations in air. Specifically, BDE-47 and 99 showed the highest concentrations, with median concentrations in dust in the hundreds μg/g range, with air concentrations at ~ 50 ng/m^3. BDE-100, 153, EH-TBB and BEH-TEBP displayed median concentrations in dust of

several tens μg/g, and 10-25 ng/m^3 in air. Interestingly, compared with the above mentioned BFRs, concentrations of BDE-209 were not high, with a median concentration of 5 μg/g in dust, and 0.3 ng/m^3 in air. Allen et al. (2013) investigated FRs in airplane dust and found a median BDE-209 concentration around 500 μg/g, followed by ΣHBCDDs at 10 μg/g, BDE-47 and 99 at around 4 μg/g, as well as EH-TBB and BEH-TEBP at around 1 μg/g. Brown et al. (2014) investigated NBFR concentration in dust from US fire stations, finding a high concentration for EH-TBB and BEH-TEBP, with median value of 2-3 μg/g. Concentrations of other NBFRs were relatively low, with a median concentration of DBDPE 160 ng/g, BTBPE 30 ng/g, and all other NBFRs below 10 ng/g.

Generally speaking, PBDEs are more thoroughly studied than other BFRs, with data on NBFRs especially scarce. BDE-209 usually shows the highest concentration among the BFRs investigated, followed by BDE-99 and 47, especially in the US. More detailed data on BFR concentrations in indoor air and dust from previous studies are summarized in Table 1.4-1.8.

Table 1.4: Summary of concentrations of PBDEs in indoor dust, ng/g (where a value is not given, it was not reported in the study concerned)

Congener #	Country	Microenvironment Category	Median	Mean	Range	n	Reference
BDE-28	China	Home	1.8	2.2	1.0-4.5	44	Yu et al., 2012
BDE-28	Czech Republic	Car	<0.1	<0.1	<0.1	27	Kalachova et al., 2012
BDE-28/33	US	Office			<0.4-207	31	Watkins et al., 2011
BDE-28	UK	Classroom	<1	1.4	<1-2.5	43	Harrad et al., 2010
BDE-28	UK	Home	nd	0.70	nd-2.1	30	Harrad et al., 2008
BDE-28	UK	Office	nd	1.8	nd-110	18	Harrad et al., 2008
BDE-28	UK	Car	nd	6.1	ND-434	20	Harrad et al., 2008
BDE-47	Sweden	Apartment	37		<0.5-280	34	Thuresson et al., 2012
BDE-47	Canada	Home	280	560	<0.2-4900	116	Shoeib et al., 2012
BDE-47	Pakistan	Mosque	2.45	2.7	0.27-7.95	12	Ali et al., 2012b
BDE-47	UK	Classroom	26	32	1.6-120	43	Harrad et al., 2010
BDE-47	UK	Home	10	15	1.2-5.8	30	Harrad et al., 2008
BDE-47	UK	Office	23	67	2.6-380	18	Harrad et al., 2008
BDE-47	UK	Car	54	720	19-7500	20	Harrad et al., 2008
BDE-85	South Africa	Office	ND	10.7	ND-44.7	12	Kefeni and Okonkwo, 2012
BDE-85	Denmark	Home	0.538	3.04	<LOQ-67.0	42	Vorkamp et al., 2011
BDE-85	UK	Classroom	1.1	2.8	<1-20	43	Harrad et al., 2010
BDE-99	US	Airplane floor	950		330-37000	40	Allen et al., 2013

Congener #	Country	Microenvironment Category	Median	Mean	Range	n	Reference
BDE-99	Germany	Car			1.3-88	12	Brommer et al., 2012
BDE-99	Vietnam	Home	3.6		0.98–54	6	Nguyen Minh et al., 2013
BDE-99	UK	Classroom	36	54	1.1-270	43	Harrad et al., 2010
BDE-99	UK	Home	20	36	2.8-180	30	Harrad et al., 2008
BDE-99	UK	Office	76	120	4.2-490	18	Harrad et al., 2008
BDE-99	UK	Car	100	990	23-8000	20	Harrad et al., 2008
BDE-100	China	Home	1.1	2.8	0.6-10.3	44	Yu et al., 2012
BDE-100	Sweden	Home	5.5		0.85-33	19	Bjorklund et al., 2012a
BDE-100	US	Bedroom			19.0-1960	29	Watkins et al., 2012
BDE-100	UK	Classroom	6.6	10	<1-50	43	Harrad et al., 2010
BDE-100	UK	Home	2.4	5.6	nd-17	30	Harrad et al., 2008
BDE-100	UK	Office	3.2	16	nd-79	18	Harrad et al., 2008
BDE-100	UK	Car	17	220	nd-2300	20	Harrad et al., 2008
BDE-153	New Zealand	Home floor	4.6	8.8	0.3-58.9	33	Coakley et al., 2013
BDE-153	US	Airplane floor	230		65-5300	40	Allen et al., 2013
BDE-153	Romania	Home	0.8	4	<0.20-40	47	Dirtu et al., 2012
BDE-153	UK	Classroom	10	28	<2-310	43	Harrad et al., 2010
BDE-153	UK	Home	5.0	14	nd-110	30	Harrad et al., 2008
BDE-153	UK	Office	8.7	16	nd-99	18	Harrad et al., 2008
BDE-153	UK	Car	11	150	nd-1500	20	Harrad et al., 2008
BDE-183	Sweden	Day care centre	6.5		2.7-15	10	Thuresson et al., 2012
BDE-183	China	Home	77.7	148	14.5-797	23	Kang et al., 2011
BDE-183	US	Gym	8500		440-1870	5	Carignan et al., 2013

Congener #	Country	Microenvironment Category	Median	Mean	Range	n	Reference
BDE-183	UK	Classroom	1.2	5.1	<2-48	43	Harrad et al., 2010
BDE-183	UK	Home	4.2	71	nd-550	30	Harrad et al., 2008
BDE-183	UK	Office	8.3	110	nd-24	18	Harrad et al., 2008
BDE-183	UK	Car	7.8	19	nd-67	20	Harrad et al., 2008
BDE-209	Sweden	Home	520		190-9300	19	Bjorklund et al., 2012a
BDE-209	US	Office			912-106204	31	Watkins et al., 2011
BDE-209	China	Home	975	2458	346-15795	23	Kang et al., 2011
BDE-209	UK	Classroom	5000	8500	49-88000	43	Harrad et al., 2010
BDE-209	UK	Home	8100	260000	nd-2200000	30	Harrad et al., 2008
BDE-209	UK	Office	6200	30000	620-280000	18	Harrad et al., 2008
BDE-209	UK	Car	100000	410000	12000-2600000	20	Harrad et al., 2008

Table 1.5: Summary of concentrations of HBCDDs and TBBPA in indoor dust, ng/g

BFRs	Country	Microenvironment Category	Median	Mean	Range	n	Reference
α-HBCDD	China	Office	92	1774	6-42274	56	Ni and Zeng, 2013
β-HBCDD	China	Office	22	586.8	5-25859	56	Ni and Zeng, 2013
γ-HBCDD	China	Office	2386	4916	638-54840	56	Ni and Zeng, 2013
Σ-HBCDD	China	Office	2621	7276	652-122973	56	Ni and Zeng, 2013
TBBPA	China	Office	975	3882	30-49140	56	Ni and Zeng, 2013

BFRs	Country	Microenvironment Category	Median	Mean	Range	n	Reference
α-HBCDD	US	Home	62		17-910	16	Dodson et al., 2012
β-HBCDD	US	Home	16		7-230	16	Dodson et al., 2012
γ-HBCDD	US	Home	73		13-790	16	Dodson et al., 2012
Σ-HBCDD	US	Home	160		39-1800	16	Dodson et al., 2012
TBBPA	US	Home	200		22-2000	16	Dodson et al., 2012
α-HBCDD	UK	Classroom	1400	2200	24-10000	43	Harrad et al., 2010
β-HBCDD	UK	Classroom	550	980	14-6700	43	Harrad et al., 2010
γ-HBCDD	UK	Classroom	1700	5800	34-72000	43	Harrad et al., 2010
∑HBCDDs	UK	Classroom	4100	8900	72-89000	43	Harrad et al., 2010
α-HBCDD	UK	Home	380	3200	22-66000	45	Abdallah et al., 2008
β-HBCDD	UK	Home	93	1000	9-26000	45	Abdallah et al., 2008
γ-HBCDD	UK	Home	670	4200	70-75000	45	Abdallah et al., 2008
Σ-HBCDD	UK	Home	1300	8300	140-140000	45	Abdallah et al., 2008
TBBPA	UK	Home	62	87	ND-382	35	Abdallah et al., 2008
α-HBCDD	UK	Office	220	610	15-2900	28	Abdallah et al., 2008
β-HBCDD	UK	Office	84	210	11-1300	28	Abdallah et al., 2008
γ-HBCDD	UK	Office	470	760	36-3700	28	Abdallah et al., 2008
Σ-HBCDD	UK	Office	760	1600	90-6600	28	Abdallah et al., 2008
TBBPA	UK	Office	36	49	ND-140	28	Abdallah et al., 2008
α-HBCDD	UK	Cars	2000	3200	54-8800	20	Abdallah et al., 2008
β-HBCDD	UK	Cars	740	1400	16-5200	20	Abdallah et al., 2008
γ-HBCDD	UK	Cars	9600	14000	27-56000	20	Abdallah et al., 2008
Σ-HBCDD	UK	Cars	13000	19000	190-69000	20	Abdallah et al., 2008

BFRs	Country	Microenvironment Category	Median	Mean	Range	n	Reference
TBBPA	UK	Cars	2	6	ND-25	20	Abdallah et al., 2008
α-HBCDD	UK	Public	1000	1000	810-1200	4	Abdallah et al., 2008
β-HBCDD	UK	Public	310	330	270-420	4	Abdallah et al., 2008
γ-HBCDD	UK	Public	1300	1400	1100-1700	4	Abdallah et al., 2008
Σ-HBCDD	UK	Public	2700	2700	2300-3200	4	Abdallah et al., 2008
TBBPA	UK	Public	230	220	52-350	4	Abdallah et al., 2008

Table 1.6: Summary of concentrations of NBFRs in indoor dust, ng/g

NBFRs	Country	Microenvironment Category	Median	Mean	Range	n	Reference
HCDBCO	US	Home	<5		<5-72	16	Dodson et al., 2012
HCDBCO	Romania	Home	<2		<2-18	47	Dirtu et al., 2012
PBEB	Canada	Home		0.50	<0.07-4.1	116	Shoeib et al., 2012
PBEB	Czech Republic	Home	<1.0	<1.0	<1.0	25	Kalachova et al., 2012
PBEB	Czech Republic	Car	<1.0	<1.0	<1.0	27	Kalachova et al., 2012
EH-TBB	US	Airplane floor	350		200-3000	40	Allen et al., 2013
EH-TBB	US	Home	100		45-5900	16	Dodson et al., 2012
EH-TBB	Romania	Home	<2	3	<2-21	47	Dirtu et al., 2012

NBFRs	Country	Microenvironment Category	Median	Mean	Range	n	Reference
EH-TBB	New Zealand	Floor	2	4	<2 – 2,285	34	Ali et al., 2012a
EH-TBB	New Zealand	Mattress	3	4	<2 – 40	16	Ali et al., 2012a
EH-TBB	UK	Classroom	25	45	<2-289	36	Ali et al., 2011a
BEH-TEBP	US	Gym	30000		17300-44900	5	Carignan et al., 2013
BEH-TEBP	Pakistan	Home	3.46	7.33	<0.2-141	31	Ali et al., 2012b
BEH-TEBP	Pakistan	Mosque	5.23	5.12	<0.2-31	12	Ali et al., 2012b
BEH-TEBP	New Zealand	Floor	12	20	<2 – 640	34	Ali et al., 2012a
BEH-TEBP	New Zealand	Mattress	1	10	<2 – 50	16	Ali et al., 2012a
BEH-TEBP	UK	Classroom	96	381	<2-6175	36	Ali et al., 2011a
BTBPE	Czech Republic	Home	<2.0	3	<2.0–21.5	25	Kalachova et al., 2012
BTBPE	Czech Republic	Car	<2.0	1	<2.0–13.9	27	Kalachova et al., 2012
BTBPE	US, California	Home	12		3-130	16	Dodson et al., 2012
BTBPE	Romania	Home	4	9	<2-90	47	Dirtu et al., 2012
BTBPE	Pakistan	Home	3.13	10	<0.2-397	31	Ali et al., 2012b
BTBPE	Pakistan	Mosque	2.16	4.93	<0.2-52	12	Ali et al., 2012b
BTBPE	New Zealand	Floor	2	3	<2 – 175	34	Ali et al., 2012a
BTBPE	New Zealand	Mattress	1	3	<2 – 37	16	Ali et al., 2012a
BTBPE	Czech Republic	Home	<2.0	3	<2.0–21.5	25	Kalachova et al., 2012
BTBPE	Canada	Home	30	65	1.8-610	116	Shoeib et al., 2012
BTBPE	UK	Classroom	9	78	<0.5-1741	36	Ali et al., 2011a

NBFRs	Country	Microenvironment Category	Median	Mean	Range	n	Reference
BTBPE	UK	Home	5.3	120	nd-1900	30	Harrad et al., 2008
BTBPE	UK	Office	nd	7.2	nd-40	18	Harrad et al., 2008
BTBPE	UK	Car	nd	7.7	nd-29	20	Harrad et al., 2008
DBDPE	Czech Republic	Home	140.8	230.8	<20.0–1698.6	25	Kalachova et al., 2012
DBDPE	Czech Republic	Car	98.8	268.7	<20.0–3566.6	27	Kalachova et al., 2012
DBDPE	Germany	Car		1300	110-6500	12	Brommer et al., 2012
DBDPE	Germany	Home		40	30-66	6	Brommer et al., 2012
DBDPE	Germany	Office		90	21-210	10	Brommer et al., 2012
DBDPE	Pakistan	Home	13.9	32.5	5.05-850	31	Ali et al., 2012b
DBDPE	Pakistan	Mosque	14.6	15.6	<5-296	12	Ali et al., 2012b
DBDPE	New Zealand	Floor	23	30	<2 – 1430	34	Ali et al., 2012a
DBDPE	New Zealand	Mattress	9	16	<5 – 220	16	Ali et al., 2012a
DBDPE	UK	Classroom	98	293	<20-2467	36	Ali et al., 2011a
DBDPE	UK	Home	24	270	nd-3400	30	Harrad et al., 2008
DBDPE	UK	Office	99	170	nd-860	18	Harrad et al., 2008
DBDPE	UK	Car	100	400	nd-2900	20	Harrad et al., 2008
TBBPA-BDBPE	US	Home	7		<10-560	16	Dodson et al., 2012
TBBPA-BDBPE	UK	Classroom	107	729	<20-9961	36	Ali et al., 2011a

Table 1.7: Summary of concentrations of PBDEs in indoor air, pg/m^3

Congener #	Country	Microenvironment Category	Median	Mean	Range	n	Reference
BDE-28	Sweden	Apartment	4.5		0.086-110	19	Bjorklund et al., 2012b
BDE-28	Sweden	Office	1.3		0.042-14	20	Bjorklund et al., 2012b
BDE-28	Sweden	Day care centre	0.042		0.042-10	5	Bjorklund et al., 2012b
BDE-47	Sweden	Apartment	17		4.1-1100	19	Bjorklund et al., 2012b
BDE-47	Sweden	Office	240		23-370	20	Bjorklund et al., 2012b
BDE-47	Sweden	Day care centre	34		4.2-200	5	Bjorklund et al., 2012b
BDE-99	Sweden	Apartment	5.2		0.78-220	19	Bjorklund et al., 2012b
BDE-99	Sweden	Office	320		4.4-560	20	Bjorklund et al., 2012b
BDE-99	Sweden	Day care centre	19		3.1-33	5	Bjorklund et al., 2012b
BDE-153	Sweden	Apartment	0.88		0.17-3.9	19	Bjorklund et al., 2012b
BDE-153	Sweden	Office	32		0.042-51	20	Bjorklund et al., 2012b
BDE-153	Sweden	Day care centre	1.4		0.042-3.2	5	Bjorklund et al., 2012b
BDE-183	Sweden	Apartment	1.2		0.0014-23	19	Bjorklund et al., 2012b
BDE-183	Sweden	Office	210		0.014-420	20	Bjorklund et al., 2012b
BDE-183	Sweden	Day care centre	0.31		0.014-27	5	Bjorklund et al., 2012b
BDE-209	Sweden	Apartment	27		0.70-220	19	Bjorklund et al., 2012b
BDE-209	Sweden	Office	2400		57-3600	20	Bjorklund et al., 2012b
BDE-209	Sweden	Day care centre	820		62-1400	5	Bjorklund et al., 2012b

Congener #	Country	Microenvironment Category	Median	Mean	Range	n	Reference
Σtri-hexaBDE	UK	Office	71	166	10-1416	33	Harrad et al., 2006
Σtri-hexaBDE	UK	Home	24	52	4-245	31	Harrad et al. 2006
Σtri-hexaBDE	UK	Car	41	709	11-8184	25	Harrad et al. 2006
Σtri-hexaBDE	UK	Public	144	112	29-162	3	Harrad et al. 2006
BDE-47	UK	Car cabin	56	136	7-671	20	Abdallah and Harrad, 2010
BDE-99	UK	Car cabin	51	128	8-588	20	Abdallah and Harrad, 2010
BDE-100	UK	Car cabin	7	36	<0.3-283	20	Abdallah and Harrad, 2010
BDE-153	UK	Car cabin	11	29	<0.4-166	20	Abdallah and Harrad, 2010
BDE-183	UK	Car cabin	15	32	<0.4-171	20	Abdallah and Harrad, 2010
BDE-209	UK	Car cabin	1300	1700	200-4000	20	Abdallah and Harrad, 2010
BDE-47	UK	Car trunk	63	126	16-419	19	Abdallah and Harrad, 2010
BDE-99	UK	Car trunk	61	112	9-394	19	Abdallah and Harrad, 2010
BDE-100	UK	Car trunk	8	26	<0.3-102	19	Abdallah and Harrad, 2010
BDE-153	UK	Car trunk	18	23	<0.4-123	19	Abdallah and Harrad,

Congener #	Country	Microenvironment Category	Median	Mean	Range	n	Reference
							2010
BDE-183	UK	Car trunk	18	28	<0.4-97	19	Abdallah and Harrad, 2010
BDE-209	UK	Car trunk	900	1200	90-3700	19	Abdallah and Harrad, 2010
BDE-28	Germany	Home	4.21	5.58	1.06-17.2	34	Fromme et al., 2009
BDE-47	Germany	Home	9.39	19.1	3.17-169	34	Fromme et al., 2009
BDE-99	Germany	Home	2.65	9.66	<0.52-189	34	Fromme et al., 2009
BDE-100	Germany	Home	0.54	1.93	<0.23-33.3	34	Fromme et al., 2009
BDE-153	Germany	Home	0.27	1.24	<0.08-22.8	34	Fromme et al., 2009
BDE-183	Germany	Home	0.44	1.40	<0.14-21.5	34	Fromme et al., 2009
BDE-209	Germany	Home	9.50	33.3	0.87-438	34	Fromme et al., 2009
BDE-47	Canada	Home	66	160	ND-1600	55	Zhu et al., 2008
BDE-99	Canada	Home	15	42	ND-890	55	Zhu et al., 2008

Table 1.8: Summary of HBCDDs, TBBPA and HCDBCO concentrations in indoor air, pg/m^3

BFRs	Country	Microenvironment Category	Median	Mean	Range	n	Reference
α-HBCDD	UK	Car cabin	87	90	14-178	20	Abdallah and Harrad, 2010
β-HBCDD	UK	Car cabin	39	40	7-74	20	Abdallah and Harrad, 2010
γ-HBCDD	UK	Car cabin	250	237	49-493	20	Abdallah and Harrad, 2010
TBBPA	UK	Car cabin	3	3	<0.2-5	20	Abdallah and Harrad, 2010
α-HBCDD	UK	Car trunk	94	108	29-234	19	Abdallah and Harrad, 2010
β-HBCDD	UK	Car trunk	46	59	17-158	19	Abdallah and Harrad, 2010
γ-HBCDD	UK	Car trunk	217	260	115-479	19	Abdallah and Harrad, 2010
TBBPA	UK	Car trunk	1	1	<0.2-3	19	Abdallah and Harrad, 2010
α-HBCDD	UK	Home	37	59	14-430	33	Abdallah et al., 2008
β-HBCDD	UK	Home	22	22	5-54	33	Abdallah et al., 2008
γ-HBCDD	UK	Home	120	170	39-710	33	Abdallah et al., 2008
Σ-HBCDD	UK	Home	180	250	67-1300	33	Abdallah et al., 2008
TBBPA	UK	Home	15	16	9-22	33	Abdallah et al., 2008

BFRs	Country	Microenvironment Category	Median	Mean	Range	n	Reference
α-HBCDD	UK	Office	36	43	18-87	25	Abdallah et al., 2008
β-HBCDD	UK	Office	23	24	14-34	25	Abdallah et al., 2008
γ-HBCDD	UK	Office	110	120	43-370	25	Abdallah et al., 2008
Σ-HBCDD	UK	Office	170	180	70-460	25	Abdallah et al., 2008
TBBPA	UK	Office	11	16	4-33	25	Abdallah et al., 2008
α-HBCDD	UK	Public place	210	250	180-400	4	Abdallah et al., 2008
β-HBCDD	UK	Public place	24	28	19-46	4	Abdallah et al., 2008
γ-HBCDD	UK	Public place	570	550	360-690	4	Abdallah et al., 2008
Σ-HBCDD	UK	Public place	900	900	820-960	4	Abdallah et al., 2008
TBBPA	UK	Public place	27	26	17-32	4	Abdallah et al., 2008
HCDBCO	Canada	Home	92	240	ND-3000	55	Zhu et al., 2008

1.2.1.2 BFRs in the outdoor environment

BFRs can enter the outdoor environment via emissions such as factory effluents and waste treatment, and by air exchange with the indoor environment. Due to their high K_{ow} value and low water solubility, BFRs mainly bind with airborne particulate matter following emissions to the atmosphere and sediment after entering the water system. Because of this, studies on BFRs in water are relative scarce. Yang et al. (2014) investigated concentrations of tri-to-hexa-BDEs in 9 English lakes between 2008 and 2012, obtaining a concentration of ΣPBDEs ranging from 10 to 200 pg/L, with a mean value of 60 pg/L. Venier et al. (2014) measured concentrations of PBDEs, HBCDDs, and NBFRs in the Great Lakes, finding that the mean concentration of ΣPBDEs were of the 10-100 pg/L level. Concentrations of ΣHBCDDs and ΣNBFRs were even lower, in most lakes lower than 10 pg/L. Harrad et al. (2009) measured concentrations of TBBPA and HBCDDs in English lake water and sediment. The concentration ranges for TBBPA were 140-3200 pg/L in water, and 0.3-4 ng/g dw in sediment, and corresponding data for ΣHBCDDs were 80-270 pg/L and 0.9-5 ng/g dw. Barón et al. (2014) measured concentrations of tetra- to deca-BDEs and DBDPE in river sediment in Spain, and concentration range for ΣPBDEs and DBDPE were nd-40 ng/g dw and nd-30 ng/g dw, respectively. Zhang et al. (2015) measured BFR concentrations in Pearl River sediment, and found the concentration ranges were 1-200, 0.4-35 and nd-0.8 ng/g dw for ΣPBDEs, DBDPE and BTBPE, respectively. Gallen et al. (2016) investigated PBDE and HBCDD concentrations in landfill leachate of Australia and found that

BDE-47 and 99 were the major BFRs, ranging from 1 to 900 ng/L. The maximum concentration of HBCDDs, BDE-183 and BDE-209 were 9.3, 110 and 180 ng/L, respectively. Contamination of landfill leachate may further lead to contamination of soil and groundwater.

Soil is an important sink for BFRs due to its high organic content and sorption capacity. Especially, extremely high BFR concentrations were found in soil around e-waste recycling site and BFR production factory. Leung et al. (2007) investigated soil PBDE concentrations in e-waste recycling site of Guiyu, China, finding ΣPBDE concentration ranged from 2700 to 4000 ng/g dw. In soils around a PBDE production area of Laizhou Bay, China, ΣPBDE concentration was reported ranging between 70-2600 ng/g dw (Jin et al., 2011). Zhu et al. (2017) investigated HBCDD concentrations around an expanded polystyrene (EPS) manufacturing factory, and ΣHBCDD concentrations were found to be 300-300,000 ng/g dw, 3-1700 ng/g dw and 20-700 ng/g dw in dust, soil and sediment, respectively. They further identified the EPS factory as an important point source for HBCDDs in the vicinal environment. Desborough et al. (2016) measured HBCDD concentrations in UK and Australia soils, finding significantly higher ΣHBCDD concentrations in the UK (median 0.73 ng/g dw, range <0.01-430 ng/g dw, n=24) compared to Australia (median 0.10 ng/g dw, range <0.0002-5.6 ng/g dw, n=17).

Harrad and Hunter (2006) measured tri- to hexa-BDE concentrations in air and soil

along a prevailing wind direction transect in the West Midlands conurbation, UK between 2003 and 2004. Concentration range for $\Sigma BDE_{28:154}$ was 3-23 pg/m^3 in air, and 70-4000 pg/g dw in soil. Drage et al. (2016) conducted a study following Harrad and Hunter (2006) along a similar transect between 2012 and 2013 with a wider BFR spectrum, and reported mean (range) concentrations of 150 (90-370), 50 (7-66) and 100 (60-130) pg/m^3 for BDE-209, $\Sigma BDE_{17:183}$ and ΣHBCDDs respectively in air, and 11 (1-45), 3.6 (1.5-5.8) ng/g organic matter for BDE-209 and $\Sigma BDE_{17:183}$ in soil. Harrad et al. (2004) also conducted another study to compare PBDE concentrations between indoor and outdoor air in the UK, finding a much higher concentration in indoor air ($\Sigma BDE_{28:154}$ ranged between 60-5700 pg/m^3, mean 760 pg/m^3) than in outdoor (ranged 10-33 pg/m^3, mean 18 pg/m^3). However, the relative concentration in indoor and outdoor air was slightly different in China, as reported by Ding et al. (2016), who investigated concentrations of PBDEs and DBDPE in paired indoor and outdoor air samples from Guangzhou. They found that concentrations of Penta- and Octa-BDE were higher in indoor air than outdoors, while concentrations of Deca-BDE and DBDPE were higher in outdoor air. BDE-209 accounted for the majority of PBDEs, with median concentration 70 and 450 pg/m^3 in indoor and outdoor air, respectively. Nevertheless, median concentrations of Penta- and Octa-BDE were only around 2-5 pg/m^3 for both compartments. Concentrations of DBDPE were of the same order of magnitude as BDE-209, with median values of 75 and 130 pg/m^3 in indoor and outdoor air respectively.

1.2.2 Biotic occurrence

The lipophilicity of BFRs favours their accumulation in fatty tissues, and thus their accumulation via the food chain. Harrad et al. (2009) investigated concentrations of TBBPA and HBCDDs in English lake water and fish, reporting concentration range of <0.29-1.7 ng/g lipid for TBBPA, and 14-290 ng/g lipid for ΣHBCDDs in fish. Based on their data, they further calculated bioaccumulation factors to be 5900, 1300, 810, and 2100 for α-, β-, γ- and ΣHBCDDs, respectively. In the research of Zhu et al. (2017), concentrations of ΣHBCDD were found to be 4-45 ng/g dw, 2-10 ng/g dw and 0.9-10 ng/g dw in fish, shrimps and crabs, respectively in Bohai Bay, China. They further estimated the trophic magnification factor for HBCDD was close to 2. HBCDDs were also detected in plant leaves and barks, ranging between 3.5-2500 ng/g dw. (Guo et al., 2017) investigated 60 FRs in Great Lakes fishes, finding that PBDEs were the most abundant FRs, with a mean concentration of 250 ng/g lipid. Moreover, BFRs with 3-6 bromines were found to be more bioaccumulative than higher molecular weight congeners.

Chen and Hale (2010) reviewed PBDE contamination globally and found that birds utilizing terrestrial and aquatic food webs showed distinctly different PBDE profile patterns. Elevated PBDE burdens were found in North American aquatic birds, possibly due to greater use of Penta-BDE there. Deca-BDE, however, showed a highest concentration in North American and Chinese terrestrial birds, which arise as a

consequence of urbanization and e-waste recycling. Biomagnification factors (BMFs) of PBDEs in various food chains were also summarised by Chen and Hale (2010) with BMFs ranging from 0.4 to higher than 400, with most BMFs between 5-40. Jorundsdottir et al. (2013) investigated PBDEs and HBCDDs in eggs of 7 marine birds from the sub-Arctic region of the Atlantic. ΣPBDE concentrations ranged from 44 to 2400 ng/g fat, with ΣHBCDD concentrations ranging from 1.3 to 41 ng/g fat. Labunska et al. (2013) investigated PBDEs in duck eggs in Eastern China and found that ΣPBDE concentrations ranged from 50 to 1800 ng/g lipid near e-waste recycling sites. In contrast, concentrations in eggs from a control site were only 8 ng/g lipid.

BFRs can also enter biota via indoor contamination. Guo et al. (2012) investigated PBDE concentrations in house cat serum of California, US and found PBDE concentrations in California house cat serum were extremely high, with a median ΣPBDEs concentration of 2,900 ng/g lipid, ranging from 630 to 23,000 ng/g lipid. They further demonstrated that the main exposure source to the cats was house dust.

1.3 Toxicity

The toxicity of BFRs was first realized following an accident on a farm in Michigan in 1973, when food for livestock was contaminated by PBBs (D'Silva et al., 2004). A toxic syndrome was observed in the exposed livestock and production of PBBs was largely ceased from that point. To date, more and more evidence show toxic concerns for not only PBBs, but also many other BFRs. Alteration of thyroid hormone level and/or

relative gene expression were observed in e-waste recycling workers (Zheng et al., 2017), fish (Arkoosh et al., 2017; Nugegoda and Kibria, 2017), amphibians (Yost et al., 2016), birds (Fernie and Marteinson, 2016) and mice (Sarkar et al., 2016) that were exposed to PBDEs. Zhao et al. (2014) observed neurotoxicity in rat offspring prenatally co-exposed to low doses of BDE-99 and methylmercury, while Wang et al. (2015) reported neurotoxicity of PBDEs to zebra fish. Costa et al. (2014) inferred there might be both direct and indirect mechanisms of neurotoxicity for PBDEs. The direct mechanisms included oxidative stress leading to DNA damage and apoptotic cell death whilst the indirect pathways may work via thyroid hormone disruption. Moreover, reproductive effects of PBDEs were indicated by some epidemiological studies (Gao et al., 2016; Makey et al., 2016).

HBCDDs affect the thyroid system by altering expression of biotransformation enzymes (Marvin et al., 2011). American Chemistry Council (2011) (cited by Marvin et al., 2011) found thyroid hyperplasia and lower serum thyroixine (T4) concentration in HBCDD treated rats, while van der Ven et al. (2009) found effects on both the thyroid system and liver of HBCDD fed rats. Palace et al. (2008) observed thyroid axis disruption in HBCDD exposed juvenile rainbow trout. Fernie et al. (2009) found delayed egg laying, deceased egg size, eggshell thinning and reduced fertility of American kestrels exposed to HBCDDs.

TBBPA can affect the thyroid system due to a very similar structure to T4 (de Wit, 2002). Meerts et al. (2000) demonstrated a strong competitive binding property of TBBPA to transthyretin and adverse effect on thyroid system and neurological function was observed by Van der Ven et al. (2008). Besides effects on thyroid hormones, Kitamura et al. (2002) also found estrogenic activity of TBBPA.

Data regarding NBFR toxicity are very limited. Structurally similar to BDE-209, DBDPE was also found to influence the thyroid hormone system (Wang et al., 2010). Specifically, Wang et al. (2010) found increased triiodothyronine (T3) levels in male rats treated with DBDPE. Further, Johnson et al. (2013) investigated the relationship between male human serum hormone levels and BFR concentrations in house dust, finding a positive relationship between the thyroid hormone T3 and concentrations in house dust of BTBPE and BEH-TEBP.

To summarize, toxicity concerns on BFRs are mainly chronic effects on the endocrine system, especially the thyroid system, reproductive system and neurodevelopment. Acute toxicity however, is of less concern at the concentrations commonly occurring in the environment.

1.4 Exposure pathways

Considering the ubiquitous occurrence and toxicity of BFRs, great concerns have been raised regarding the human health risks of BFRs. To better evaluate such health risks,

a number of studies investigating BFR exposure and body burden have carried out. It has now widely been acknowledged that humans may be exposed to BFRs via 4 pathways: diet, dust ingestion, air inhalation and dermal contact with dust and BFR-containing items (Abdallah et al., 2008; Besis and Samara, 2012; Covaci et al., 2011; Daso et al., 2010; Johnson-Restrepo and Kannan, 2009; Trudel et al., 2011; Webster et al., 2015). However, the detailed contribution of each of these pathways varies substantially among different compounds, individual life styles and nations (Abdallah and Harrad, 2009; Covaci et al., 2011). Generally speaking, air inhalation is of less importance compared with diet and dust ingestion (Besis and Samara, 2012, Webster et al., 2015), while little is known about dermal exposure due to practical difficulties in studying such exposure (Abdallah et al., 2015c). Besis and Samara (2012) reviewed PBDE exposure via dust ingestion, air inhalation and dietary intake among countries, summarizing that dietary intake stayed between 50-70 ng/day, while dust ingestion could vary from 10 ng/day to more than 200 ng/day. Air inhalation, in all countries, was of least significance of the different pathways considered. Tao et al. (2017) estimated the daily intake of several NBFRs including EH-TBB, BEH-TEBP, BTBPE, DBPDE and tetrabromoethylcyclohexane (DBE-DBCH) by UK adults via dust ingestion, diet and air inhalation, reporting median ΣNBFRs intake to be 11, 80 and 3 ng/day via dust ingestion, diet and air inhalation, respectively.

Barghi et al. (2016) investigated HBCDD concentrations in more 500 food samples in

Korea, reporting a ΣHBCDD concentration ranging from not detected to 4.90 ng/g ww. Higher ΣHBCDD concentrations and α-HBCDD abundance were found in animal based foods. Dietary intake of HBCDDs was observed to decrease with increasing age, from 2.9 ng/kg bw/day to 0.6 ng/kg bw/day, with an average intake of 0.8 ng/kg bw/day. Coelho et al. (2016) investigated PBDE, HBCDD and NBFR (BTBPE, DBDPE and DBE-DBCH) in 21 seven-day Portuguese duplicate samples, finding PBDE and HBCDD levels were low, or even below limit of detection in most samples, and NBFRs not detected in all samples. Upper bound dietary intakes were estimated at 560-1200 (median 650) ng/day for ΣPBDEs, and 32-2200 (median 40) ng/day for ΣHBCDDs, and lower bound 0-440 (median 67) ng/day for ΣPBDEs, 0-2200 (median 0) ng/day for ΣHBCDDs. Shi et al. (2016) measured 6 NBFRs in a total of 80 food composite and human milk samples across 20 provinces of China, claiming that DBDPE had become one of the main BFRs used in China with levels higher than PBDEs in food and human milk. The lower bound dietary intake of NBFRs for a "standard Chinese man" was 3.5 ng/kg bw/day, of which nearly 3.4 ng/kg bw/day was DBDPE. Dietary intake of infants via human milk was even higher than adult, which was 30 ng/kg bw/day. Tao et al. (2017) measured concentrations of PBDEs, HBCDDs and 5 NBFRs (EH-TBB, BEH-TEBP, BTBPE, DBPDE and DBE-DBCH) in UK human milk and foodstuffs, estimating average dietary intakes of BFRs to be 1.8 and 4.2 ng/kg bw/day (ΣPBDEs), 0.44 and 0.88 ng/kg bw/day (ΣHBCDDs), 1.3 and 2.6 ng/kg bw/day (ΣNBFRs), for adults and toddlers respectively. Moreover, based on the concentration data of human

milk, they estimated dietary intake of infants via breast milk to be 35, 17 and 18 ng/kg bw/day for ΣPBDEs, ΣHBCDDs and ΣNBFRs, respectively.

Cequier et al. (2014) investigated FR contamination in Norwegian indoor environments, and estimated relevant exposure via air inhalation, dust ingestion and dermal contact with dust. Exposure of ΣPBDEs were 55, 140 and 990 pg/kg bw/day via air inhalation, dermal contact with dust, and dust ingestion respectively for children, and 19, 91 and 370 pg/kg bw/day for women. Besides PBDEs, BEH-TEBP and DBDPE also showed high exposure potential, with dermal contact exposure ranging around several tens pg/kg bw/day and dust ingestion several hundred pg/kg bw/day. Lim et al. (2014) investigated indoor PBDE exposure for elementary school students in Korea, concluding that exposure in the home accounted for 80 % of total indoor exposure, followed by 16 % in elementary school. Exposure to ΣPBDEs via air inhalation, dermal dust contact and dust ingestion were around 1, 150 and 3000 pg/kg bw/day. Harrad et al. (2008) estimated daily PBDE, DBDPE and BTBPE exposure via dust ingestion for UK adults and toddlers based on their results of target BFR concentrations in home, office and car dust. According to their estimation, median BDE-209 exposure under a mean dust ingestion scenario was 233 ng/day for adults, and 610 ng/day for toddlers, while under a high dust ingestion scenario the exposure came to 580 and 2400 ng/day. Compared with BDE-209, ingestion of other BFRs were negligible, with median exposure ranging from 0.1 to 10 ng/day. Sun et al. (2016) measured PBDE

concentrations in indoor dust and air of Zhejiang, China, and estimated resultant exposure. ΣPBDE exposures for adults in the home were estimated as 10, 100 and 50 pg/kg bw/day via air inhalation, dust ingestion and dermal contact with dust, respectively. For toddlers, the corresponding data were 70, 2,400 and 170 pg/kg bw/day. Similar to the results of Harrad et al. (2008), BDE-209 accounted for more than 95 % of the ΣPBDE exposure, but the exposure level was much lower, assuming a 70 kg body weight for adults and 10 kg for toddlers. Among the three exposure pathways estimated, dust ingestion contributed the most, with air inhalation of a similar level to dust dermal contact for tri-hepta BDEs, but lower for BDE-209. Abdallah et al. (2008) estimated HBCDD and TBBPA exposure to UK adults and toddlers via air inhalation, dust ingestion and diet. Average ΣHBCDD exposure for adults was 5.0, 130 and 400 ng/day via air inhalation, dust ingestion and diet respectively; while corresponding data for toddlers were 1.0, 400 and 240 ng/day. For TBBPA, the data were 0.3, 1.6 and 2.8 ng/day for adults and 0.1, 4.4 and 0.4 ng/day for toddlers. These data imply that dust ingestion and diet are more important exposure pathways than air inhalation for both HBCDD and TBBPA. Tao et al. (2016) measured concentrations of PBDEs, HBCDDs and 16 NBFRs in UK air and dust, estimating the exposure were 280 (ΣPBDEs), 25 (ΣHBCDDs) and 38 (ΣNBFRs) ng/day via dust ingestion for toddlers, and 100, 15, 27 ng/day for adults. Exposure via air inhalation was much lower, at 0.43, 0.14 and 0.66 ng/day for toddlers, and 2.0, 2.1 and 2.3 ng/day for adults for ΣPBDEs, ΣHBCDDs, and ΣNBFRs respectively.

In most previous studies estimating exposure via dermal contact with dust, a fixed absorption factor in skin was assumed for all FRs (Cequier et al. 2014; Kim et al., 2014; Sun et al., 2016). However, experiments carried out on *in vitro* cultured human skin models indicate that such a fixed absorption factor is likely an oversimplification. Frederiksen et al. (2016) investigated dermal uptake of NBFRs using a human *ex vivo* skin model, finding little or no NBFRs penetration of skin, but significant deposition within the skin. Abdallah et al. (2015a, b) and Pawar et al. (2017) carried out a series of experiments to evaluate FR (PBDE, HBCDD, TBBPA and OPFR) dermal uptake using both *in vitro* and *ex vivo* human skin models and obtained similar results for both. Abdallah et al. (2015a, b) found the permeability coefficient differed substantially between FRs, with decreased permeation observed with increased K_{ow} and increased bromination, consistent with the findings of Frederiksen et al. (2016). In addition, both Frederiksen et al. (2016) and Abdallah et al. (2015a, b) observed a time lag of skin permeation following exposure. Further data are needed to fully understand dermal exposure.

1.5 BFR concentrations in human tissues

As demonstrated above, BFRs are ubiquitous in our living environment and food, sometimes in high concentration, and we are exposed to BFRs via various pathways, so it is not surprising that BFRs are reported to be detected in the human body. Eskenazi et al. (2011) measured serum PBDE concentrations in more than 500 Latino US and

Mexican children aged 5-7 years, finding a much higher serum PBDE level in children living in US than Mexico. The ΣBDE(-28, 47, 85, 99, 100, 153, 154) concentrations were 6-1,000 ng/g lipid (median 90 ng/g lipid) and 1-500 ng/g lipid (median 10 ng/g lipid) in US and Mexican children, respectively. BDE-47 showed a highest concentration in both US and Mexican children, with median concentrations of 47 ng/g lipid and 4.8 ng/g lipid respectively. In the northeastern US, Carignan et al. (2013) investigated serum Penta-BDE concentrations in 11 female gymnasts aging 18-22 years old, reporting a Penta-BDE concentration ranging between 40 to 400 ng/g lipid (geometric mean 110 ng/g lipid), with BDE-47 the most abundant congener (15-190 ng/g lipid, geometric mean 44 ng/g lipid). These concentrations are much higher than observed in the general US population, and they attributed this to a higher Penta-BDE concentration in gym air and dust, due to the large volumes of Penta-BDE treated polyurethane foam present in gyms. Carignan et al. (2012) conducted another study in the same area focusing on TBBPA and HBCDD concentrations in human milk and found HBCDDs in all samples, with concentration ranges of 250-4430 (geometric mean 710), 30-1640 (GM 80) and 70-3200 (GM 200) pg/g lipid weight for α-, β-, and γ-HBCDD respectively. The detection frequency for TBBPA was lower (35 %), and concentration ranged <30-550 pg/g lipid weight. In the UK, Abdallah and Harrad measured concentrations of TBBPA, HBCDDs (Abdallah and Harrad, 2011) and PBDEs (Abdallah and Harrad, 2014) in human milk. They detected HBCDDs in all samples, reporting concentrations of 0.75-20 (mean 4.9), 0.08-0.75 (mean 0.32) and

0.13-2.3 (mean 0.73) ng/g lw for α-, β-, and γ-HBCDD respectively. The detection frequency for TBBPA was 36 %, with concentration ranged <0.04-0.65 (mean 0.06) ng/g lw. Compared with the study of Carignan et al. (2012), both detection frequency and concentration ranges were very similar for all target compounds. For PBDEs, none of the hepta-nona BDEs were detected, and BDE-47 was detected in all samples as the main constituent of tri-hexa BDEs (ranging 0.2-26 ng/g lw, mean 6 ng/g lw). BDE-209 was detected in 69 % samples, with a concentration range of <0.06-0.92 (mean 0.31) ng/g lw. Tao et al. (2017) further measured NBFR concentrations (EH-TBB, BEH-TEBP, BTBPE, DBPDE and DBE-DBCH) in the same batch of human milk as Abdallah and Harrad (2011, 2014), reporting the concentration range for ΣNBFRs to be 0.57-260 (median 7.9) ng/g lw. Elsewhere, Drage et al. (2017) reported serum HBCDD concentrations in the Australian population, revealing HBCDDs to be at higher concentrations in females than in males, and lower in young children than in adults. The ΣHBCDD concentrations ranged between <0.5 to 36 ng/g lipid, with a mean of 3.1 ng/g lipid, and α-HBCDD was the dominant stereoisomer, accounting for 60 % of total concentration. In Asia, Chen et al. (2014) investigated PBDEs in 30 mother-newborn pair samples in South China, finding that ΣPBDE concentrations were 15.8 ± 9.88 ng/g lipid in placenta, 13.2 ± 7.64 ng/g lipid in breast milk, 16.5 ± 19.5 ng/g lipid in fetal cord blood, and 1.80 ± 1.99 ng/mL in neonatal urine. They found that BDE-47 was the predominant congener in all types of samples.

1.6 Legislation

Because of their wide occurrence, multiple exposure pathways, and human toxicity combined with their persistence, bioaccumulation and toxicity in eco-systems, BFRs have aroused great concern, leading to restrictions on BFR production and use worldwide. The commercial Penta- and Octa-BDE formulations have been banned worldwide and listed under the UNEP Stockholm Convention on persistent organic pollutants (POPs) since 2009 (Ashton et al., 2009). Moreover, the commercial Deca-BDE formulation has also been restricted severely in Europe since July 2008 (European Court of Justice, 2008), and was recently listed under the Stockholm Convention in May 2017 (UNEP, 2017). In addition, HBCDD was listed under Annex A of the Stockholm Convention in 2013 (UNEP, 2013).

1.7 Current knowledge gaps

As reviewed above, indoor environments as places where people spend a substantial proportion of their lives, and where myriad BFR sources exist, have attracted substantial attention. Different types of indoor environments like living rooms, bedrooms, offices, schools, kindergartens, and cars have been investigated in previous studies. However, to our knowledge no data exist about concentrations of BFRs in domestic kitchens. This is a surprising omission, given that people may spend a substantial proportion of time in this microenvironment, and that kitchens contain a substantial number of goods such as microwave ovens, dishwashers, food processors, fridges, and freezers etc. that because their plastic components represent a fuel source

in the event of fire, are likely to be flame-retarded. For this reason, it is plausible that kitchen dust and air are contaminated with BFRs and therefore exposure via dust ingestion and air inhalation are of concern.

Of additional concern is potential contamination with BFRs as a result of cooking using BFR-containing utensils, as the high temperatures and oil used in cooking may favour the transfer of BFRs into the oil. Samsonek and Puype (2013) investigated BFR concentrations in 30 black plastic food-contact articles (FCAs) and discovered high BFR (including PBDEs, TBBPA, TBBPA-BDBPE and DBDPE) concentrations in the investigated samples. Guzzonato et al. (2017) investigated 26 samples of toys and FCAs purchased from the European market, finding that ~1/3 of FCAs were Br positive and around half of the toys examined exceeded Low POP Concentration Limits (LPCLs) set by the European Commission. The high concentrations of BFRs in FCAs and toys, were likely due to the addition of recycled polymers sourced from waste electrical and electronic equipment (WEEE) during manufacturing. Despite this identified presence of BFRs in plastic FCAs, the exposure implications of this presence has yet to be investigated. Considering the wide use of recycled plastics in FCAs, attention should be paid to the potential contamination by BFRs during food preparation and cooking, as exposure may happen via utensil-food transfer, or via direct dermal contact.

Another knowledge gap is about NBFRs. Far more data are available for legacy BFRs

such as PBDEs and HBCDDs due to their longer application history and better known hazards. In contrast, research about NBFRs remains in its infancy and data are still scarce. Specifically, how NBFR use and environmental contamination differs among countries is not well known. Moreover, little is known about how recent restrictions on legacy BFRs have affected the environmental levels of both legacy and novel BFRs. Declining concentrations of legacy BFRs alongside increased NBFR concentrations are reasonable to hypothesise, as recently reported by Tao et al. (2016) in UK air and dust. However, another study of Tao et al. (2017) reported no significant temporal change in concentrations of legacy and novel BFRs in UK human milk. In summary, more data are needed to test the hypothesis.

1.8 Aims and objectives of this study

The overall aim of this study is to enhance knowledge on BFR contamination in domestic kitchens and the resultant implications for human exposure, as well as providing better information about international variations in concentrations of legacy and novel BFRs in indoor dust. The objectives thus are: 1) to report for the first time the concentrations of BFRs in kitchen dust; 2) to test the hypothesis that concentrations of BFRs in domestic kitchen dust exceed those in dust sampled simultaneously from other areas (living rooms/bedrooms) in the same houses; 3) to investigate the extent to which plastic kitchen utensils are contaminated by BFRs; 4) to evaluate the potential for exposure to BFRs while using plastic kitchen utensils; 5) to measure recent temporal trends in concentrations of legacy and novel BFRs in response to restrictions on some

legacy BFRs; 6) to evaluate differences in BFR contamination of house dust between countries; 7) to provide better knowledge about the occurrence of BFRs in indoor environments.

To achieve these objectives, we measured concentrations of 8 PBDEs (BDE-28, 47, 99, 100, 153, 154, 183 and 209), α-, β-, and γ-HBCDDs, and 5 NBFRs (PBEB, EH-TBB, BTBPE, BEH-TEBP and DBDPE), in living room dust from 7 countries (UK, Finland, Greece, Spain, Jordan, US and Mexico). Additionally, we measured concentrations of the same BFRs in 30 kitchen dust samples collected simultaneously with living room dust from the same UK houses. A hand-held X-ray fluorescence (XRF) spectrometer was applied to screen potentially flame-retarded kitchen appliances for Br, with surface wipe samples collected from appliances with high Br content and analysed for BFRs. In addition, 96 plastic kitchen utensils including spoons, spatulas, ladles etc. were collected from UK markets and families, and screened for Br using an XRF spectrometer. Of these, 30 were selected for analysis of BFRs. An experiment simulating frying food with oil was conducted to evaluate the transfer of BFRs from kitchen utensils to food when cooking. Exposure via cooking with BFR contaminated utensils was estimated based on the results of these cooking experiments, with exposure via direct dermal contact with utensils also estimated based on published transfer factors.

Chapter 2 Methodology

2.1 Sampling

2.1.1 UK kitchen and living room dust

In total, 30 homes from the West Midlands conurbation in the UK (of which Birmingham is the main city) were sampled in 2015. For each home, a dust sample from the kitchen floor was collected with a floor dust sample collected from the living room in the same house for comparison. For the 11 homes in which the living room and kitchen were in the same room, dust in the bedroom was collected instead. A nylon sock (25 mm pore size) was mounted inside the nozzle of a regular household vacuum cleaner to collect the dust. For carpeted floor, dust was collected by vacuuming a 1 m^2 area for 2 min; while for bare floors, the vacuuming area and time were 4 m^2 and 4 min, respectively. An aliquot of 2-3 g pre-baked sodium sulfate vacuumed from a clean aluminum foil surface served as a field blank in each house. All the dust samples were then sieved (500 μm mesh, UKGE Limited, UK) for ~3 minutes and stored in 30mL glass bottles at –20 °C before further analysis.

2.1.2 International living room dust

Settled house dust samples were collected by householders from domestic living rooms of Finland (Helsinki, n=20), Greece (Athens, n=10), Spain (Barcelona, n=20), Jordan (Amman, n=19), United States (Houston, n=17) and Mexico (Ciudad Victoria, n=30) from 2014 to 2015. All the samples were kept in the sampling socks, sealed in plastic

bags, and delivered to the University of Birmingham for analysis. The rest of the sampling details were the same as for the sampling of UK dust as described in 2.1.1.

2.1.3 Kitchen utensils collection

New utensils were purchased from retail outlets in Birmingham, UK between December 2015 and July 2016, while used utensils ≥ 5 years old were donated by University of Birmingham staff. All utensils were first screened for their bromine content using a hand-held XRF spectrometer (Niton^{TM} XL3t GOLDD+ XRF Analyser, Thermo Fisher Scientific) (Figure 2.1). The platform on which utensils were placed for measurement was pre-cleaned by ultra-pure water and ethanol, and measured by XRF to ensure no background interference existed. Several points on each utensil were randomly measured to avoid heterogeneity and measurement error, and the highest of the measurements made for each item recorded. All utensils showing Br content higher than 100 μg/g (n=18) were selected for further measurement of their detailed BFR content, with BFRs also measured in some utensils with Br content <100 μg/g (n=12) for comparison.

Figure 2.1: Niton™ XL3t GOLDD+ XRF Analyser, Thermo Fisher Scientific

2.1.4 Kitchen device surface wipe samples

Four domestic kitchens sampled in 2.1.1 were selected for further investigation of their BFR content in electrical kitchen goods. Every electrical device in the studied kitchens was screened for Br content by the XRF spectrometer used in 2.1.3 with a surface wipe sample taken from those containing >100 μg/g. A clinical bactericidal wipe soaked with 70 % w/w isopropyl alcohol (Williams Medical Supplies, UK) was used to wipe the surface of the device under test. The wipe was then stored in a well sealed glass bottle prior to analysis for BFRs.

2.2 Utensil-to-oil simulated cooking transfer experiment configuration

Ten kitchen utensils shown to contain elevated concentrations of BFRs were subjected to experiments designed to mimic the process of cooking in oil. A small part of each kitchen utensil under test weighing ~0.05 g, ~ 5 mm × 4 mm × 2 mm was immersed in 0.5 mL olive oil contained in a test tube. The test tube was maintained at 160 ˚C for 15 min to simulate the cooking process. This experiment was conducted in triplicate for each utensil tested.

2.3 Chemicals

Native BDE-77 was used as internal standard (IS) to quantify BDE-28, 47, 99, 100 and PBEB, EH-TBB; BDE-128 as internal standard for BDE-153, 154 and 183; ^{13}C-BTBPE for BTBPE; ^{13}C-BEH-TEBP for BEH-TEBP; ^{13}C-BDE-209 for BDE-209 and DBDPE; ^{13}C- α-, β-, γ-HBCDDs for α-, β-, γ-HBCDDs respectively. A mixed solution was prepared by dissolving all the above mentioned internal standards in iso-octane with concentration of each compound 500 pg/μL to act as internal standard solution. 2,2',3,3',4,5-Hexachlorobiphenyl (PCB-129) was used to determine the recovery of BDE-77, 128 and 128, ^{13}C-BTBPE, ^{13}C-BEH-TEBP, ^{13}C-BDE-209. The recovery determination standard (RDS) solution was prepared by dissolving PCB-129 in iso-octane with concentration of 250 pg/μL. An iso-octane solution (500 pg/μL for each solute) of all target PBDEs, NBFRs and there internal standard, recovery determination standard was used as calibration standard solution to calculate concentrations and

recoveries of target compounds. d_{18}-γ-HBCDD was used as RDS of HBCDDs and the RDS solution was prepared by dissolving d_{18}-γ-HBCDD in methanol at a concentration of 50 pg/μL. The calibration standard for HBCDDs was a mixed methanol solution of native HBCDDs, ^{13}C-HBCDDs and d_{18}-γ-HBCDD with concentration of 200 pg/μL for each solute. All standards above were purchased from Wellington Laboratories Inc and all solvents used (acetone, hexane, iso-octane, dichloromethane and methanol) were HPLC grade.

2.4 Extraction and clean up procedures

2.4.1 UK kitchen and living room dust

First, 50-100 mg dust was accurately weighed and spiked with 50 μL internal standard solution. Hexane : acetone (3:1) (2 mL) was added to the sample, which was vortexed for 60 seconds, sonicated for 5 min and centrifuged at 2000 g for 2 min. After collecting the supernatant, the residues were subjected to the same extraction process twice more. The combined supernatants were reduced in volume to ~ 2 mL under a gentle stream of nitrogen gas, before mixing with 3-4 mL 98 % sulfuric acid. The mixture was then vortexed for 20 s followed by centrifugation at 2000 g for 5 min. The supernatant was then collected. To ensure complete transfer, the residue was rinsed with hexane (2 mL) three times. The combined supernatant was then reduced to incipient dryness under a gentle stream of nitrogen gas. The final concentrate was re-dissolved in 200 μL PCB-129 solution prior to analysis of PBDEs and NBFRs by GC-MS. Following GC-MS

analysis, solvent exchange from PCB-129 iso-octane solution to d_{18}-γ-HBCDD methanol solution was conducted to facilitate determination of HBCDDs on LC-MS-MS.

2.4.2 International living room dust

An average of 50 mg dust (accurately weighed) was dispersed onto pre-cleaned Hydromatrix (Agilent Technologies, UK) in a 66 mL Dionex stainless-steel cell (Thermo Scientific, UK), and spiked with 50 μL internal standard solution. The sample was extracted at 90 °C and 1500 psi using a Dionex accelerated solvent extractor (ASE 350, Thermo Scientific, UK) for 3 static cycles with 9:1 (v:v) dichloromethane:hexane mixture (total volume ~100 mL). The crude extract was concentrated to 1 mL using a Zymark Turbovap® II and fractionated on a SPE cartridge prepacked with 1 g of florisil (Thermo Scientific, UK). The first fraction was eluted with 8 mL of hexane and the second was eluted with 15 mL of hexane:dichloromethane (1:1, v/v). The two fractions were combined and concentrated to 1 mL under a gentle stream of nitrogen gas, before mixing with 3-4 mL 98% sulfuric acid. The mixture was then vortexed for 20 s followed by centrifugation at 2000 g for 5 min. The supernatant was then collected. To ensure complete transfer, the residue was rinsed with hexane (2 mL) three times. The combined supernatant was then reduced to incipient dryness under a gentle stream of nitrogen gas. The final concentrate was re-dissolved in 200 μL PCB-129 solution prior to analysis of PBDEs and NBFRs by GC-MS. Following GC-MS analysis, solvent exchange from PCB-129 iso-octane solution to d_{18}-γ-HBCDD methanol solution was conducted to

facilitate determination of HBCDDs on LC-MS-MS.

2.4.3 Kitchen utensils

To improve the extraction efficiency, a volume reduction step for plastic utensils was conducted. Plastic utensils were first cut into small pieces and then ground into a powder by a Fritsch Pulverisette 0 cryo-vibratory micro mill (Idar-Oberstein, Germany). Each sample along with one 25 mm diameter stainless steel ball was added to the stainless steel grinding mortar (50 mL volume), and submerged in liquid nitrogen until the sample reached the temperature of the surrounding liquid (-196 °C) – the liquid nitrogen was added in small increments until the nitrogen began to be expelled from the rear vent of the mill. It was then ground at a vibrational frequency of 30 Hz for 5 min with the process repeated 2-3 times. The plastic powder was then extracted by adding 10 mL hexane, vortexing for 1 min, followed by 15 min ultrasonication. This cycle of vortexing and ultrasonication was repeated 3 times and samples were left in solvent overnight to ensure high recoveries. An acid wash as described in 2.4.1 and 2.4.2 was then applied to remove residual polymer, and the final concentrate was re-dissolved in 200 µL PCB-129 solution prior to analysis of PBDEs and NBFRs by GC-MS.

2.4.4 Cooking oil samples

The oil samples from the simulated cooking experiments were first diluted in 3~4 mL hexane, then mixed with 5~6 mL 98 % sulfuric acid. The mixture was then vortexed

for 20 s followed by centrifugation at 2000 g for 5 min. The supernatant was then collected. To ensure complete transfer, the residue was rinsed with hexane (2 mL) three times. The combined supernatant was then reduced to incipient dryness under a gentle stream of nitrogen gas. The final concentrate was re-dissolved in 200 μL PCB-129 solution prior to analysis of PBDEs and NBFRs by GC-MS.

2.4.5 Wipe samples

Wipe samples were soaked in 15 mL dichloromethane, vortexed for 2 min and then sonicated for 10 min. Extracts were then filtered through a 0.2 μm polytetrafluoroethylene filter (Rotilab®-syringe filters, Carl Roth GmbH+Co., Germany) to remove particles and fibres. To ensure the full range of compounds present was maintained, no further clean-up was carried out and the filtered extract was reduced to incipient dryness under a gentle stream of nitrogen gas. The concentrate was then re-dissolved in 0.5 mL methanol for analysis via LC-high resolution MS.

2.5 Instrumental Analysis

2.5.1 GC-ECNI-MS

A Thermo Trace 1310 gas chromatography interfaced with an ISQ single quadrupole MS equipped with a programmable-temperature vaporiser (PTV) was employed to conduct the analysis under electron capture negative ionisation (ECNI) mode. Two μL of purified sample extract were injected on a Thermo TG-SQC column (15 m×0.25 mm×0.25 μm). The injection temperature was set at 92 °C, held 0.04 min, ramp

700 °C/min to 295 °C. The GC temperature programme was initially 50 °C, held 0.50 min, ramp 20 °C/min to 240 °C, held 5 min, ramp 5 °C/min to 270 °C and then ramp 20 °C/min to 305 °C, held 16 min. Helium was used as a carrier gas with a flow rate of 1.5 mL/min for the first 22.00 min, then ramp 1.0 mL/min^2 to 2.5 mL/min, hold 13.00 min. The mass spectrometer was employed in selected ion monitoring (SIM) mode and the measured ions for each compound are listed in Table 2.1. Dwell times for each ion were 30 ms. The ion source and transfer line temperatures were set at 300 and 320 °C, respectively and the electron multiplier voltage was at 1400 V. Methane was used as reagent gas with flow rate of 1.5 mL/min. Two examples of chromatogram and mass spectrum are shown in Figure 2.2 and 2.3.

Table 2.1: Measured ions of PBDEs and NBFRs on GC-MS

Compound	Quantifier, m/z
BDE-28	79, 81
BDE-47	79, 81
BDE-77 (IS)	79, 81
BDE-99	79, 81
BDE-100	79, 81
BDE-128 (IS)	79, 81
BDE-153	79, 81
BDE-154	79, 81
BDE-183	79, 81
BDE-209	486.6, 488.6
^{13}C-BDE-209 (IS)	492.6, 494.6
PBEB	79, 81
EH-TBB	356.8, 358.8
BTBPE	330.8
^{13}C-BTBPE (IS)	336.8
BEH-TEBP	383.7, 463.7
^{13}C-BEH-TEBP (IS)	390.7, 469.7
DBDPE	79, 81
PCB-129 (RDS)	359.8, 361.8

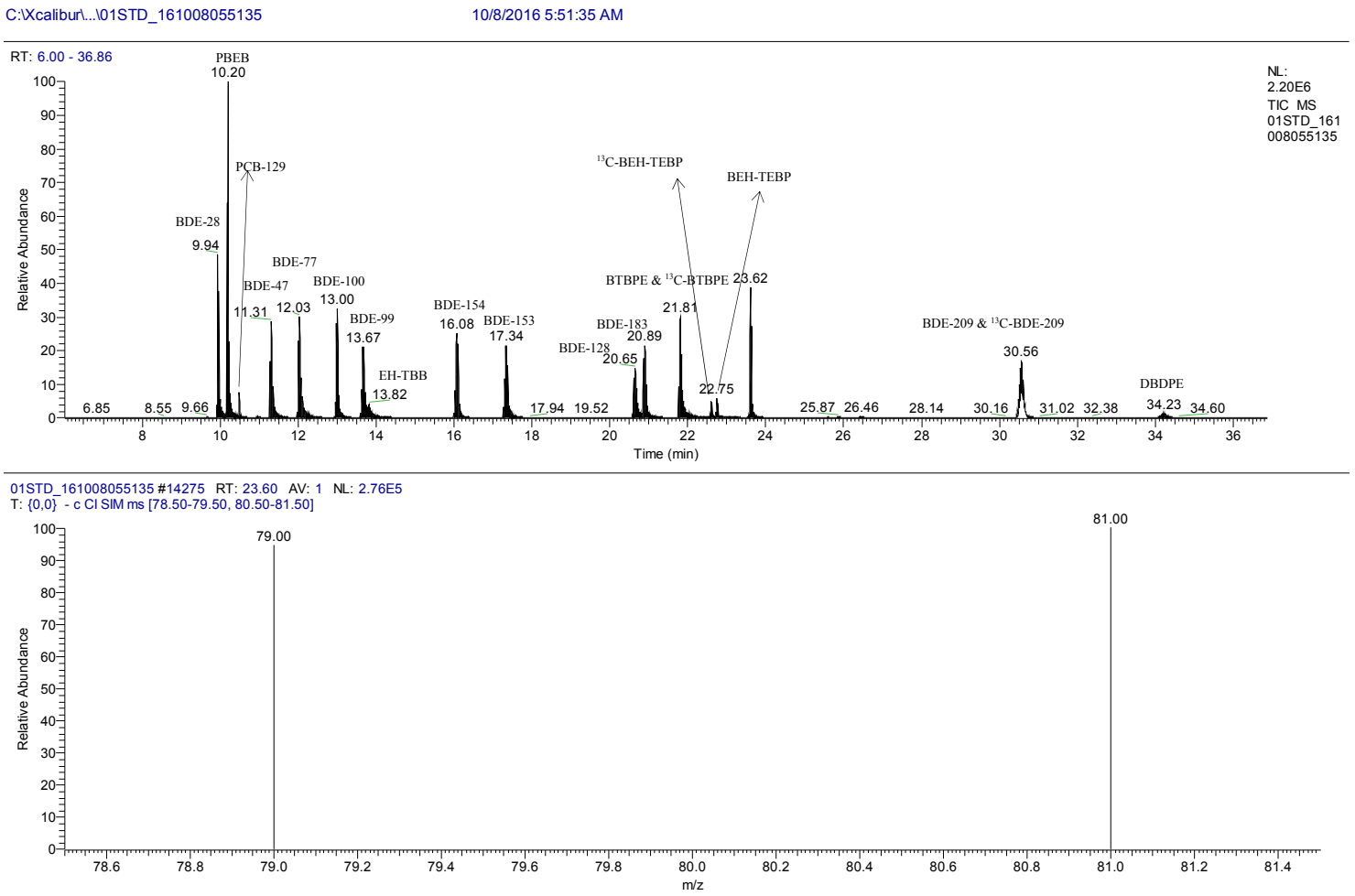


Figure 2.2: Chromatogram (upper) and mass spectrum at 23.60 min (lower) of standard solution

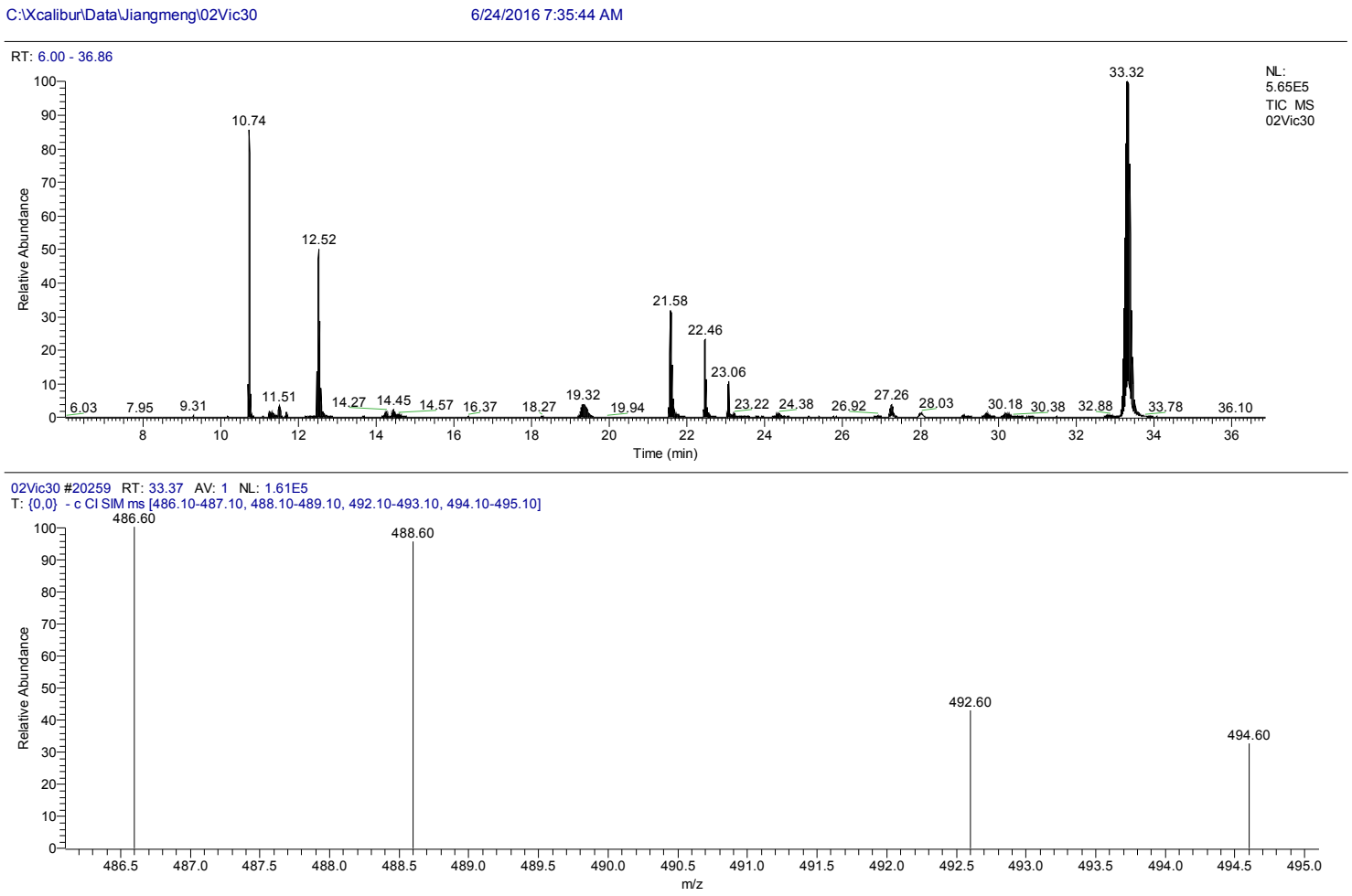


Figure 2.3: Chromatogram (upper) and mass spectrum at 33.37 min (lower) of dust sample

2.5.2 GC-EI-MS

For some plastic kitchen utensil samples with extremely high BDE-209 concentrations and their associated cooking oil extracts, recoveries of ^{13}C-BDE-209 were unreasonably high due to interference between the responses of BDE-209 (m/z 486.6, 488.6) and ^{13}C-BDE-209 (m/z 492.6, 494.6). To deal with this issue, we re-injected problematic samples under electron ionization (EI) mode, as interference between the quantifier ions of BDE-209 (m/z 799.4, 801.4) and ^{13}C-BDE-209 (809.4, 811.4) was weaker considering the greater m/z separation. All other operational parameters were the same as those deployed in ECNI mode.

2.5.3 LC-MS

High-performance liquid chromatography (HPLC, LC-20AB, SHIMADZU) followed by electrospray ionisation and tandem mass spectrometry (ESI-MS-MS, API 2000, AB Sciex) was employed to measure the concentration of HBCDDs in this study. A Varian Pursuit XRS3 C18 analytical column (150 mm × 2 mm, 3 μm particle size) was used as stationary phase, and the mobile phase was a mixture of 1:1 water and methanol (phase A) and methanol (phase B). Elution started at 50 % phase B and then increased linearly to 100 % over 4 min, held isocratically for 5 min and then decreased to 65 % over 3 min, then returned to initial condition in 0.01 min and maintained for column regeneration for another 4 min, resulting in a total run time of 16 min. The flow rate and injection volume were 0.15 mL/min and 20 μL, respectively. The mass spectra were

obtained in ESI (-) mode and data collected in MRM mode, with the parent and daughter ions for each compound listed in Table 2.2.

Table 2.2: Measured ions of HBCDDs on LC-MS-MS

Compound	Parent ion/daughter ion, m/z
α-HBCDD	640.4/78.8
^{13}C-α-HBCDD (IS)	652.4/79.0
β-HBCDD	640.4/78.8
^{13}C-β-HBCDD(IS)	652.4/79.0
γ-HBCDD	640.4/78.8
^{13}C-γ-HBCDD (IS)	652.4/79.0
d_{18}-γ-HBCDD (RDS)	657.8/78.8

2.5.4 Kitchen product wipe samples screening analysis

The screening of kitchen product surface wipe samples for their BFR content was performed on an UPLC-Orbitrap-HRMS system (Thermo Fisher Scientific, Bremen, Germany) composed of an Accela 1250 pump, and an Accela Open Auto Sampler coupled to a Q Exactive Orbitrap mass spectrometer with a separated column oven (LCO 102 single, ECOM s r. o., Czech Republic). Chromatographic separation was performed on an Accucore RP-MS column (100 x 2.1 mm, 2.6 µm) with water (mobile phase A) and methanol (mobile phase B). A gradient method at 400 µL/min flow rate was applied as follows: start at 20 % B; increase to 100 % B over 9 min, held for 3 min; then decrease to 20 % B over 0.1 min maintained for a total run time of 15 min. The injection volume was 10 µL and the column oven was set at 30 ºC. The atmospheric pressure chemical ionisation (APCI) source was used for the screening of BFRs in full scan negative mode. The parameters were set as follows: resolution 35000, AGC target 1e^6, maximum injection time 100 ms, scan range 150 to 1000 m/z, sheath gas flow rate

10, discharge current 30 μA, capillary temperature 250 ^{o}C and S-lens RF level 50. For the screening of PFRs, an electrospray ionisation (ESI) source was applied in positive mode, with sheath gas flow rate 20, discharge current 5 μA, capillary temperature 320 ^{o}C and all other parameters the same as for APCI.

2.6 QA/QC

2.6.1 UK kitchen and living room dust

As a QA/QC check, one aliquot of standard reference material SRM2585 (organics in house dust, NIST) was analysed for every 20 samples. Data obtained for these SRM analyses were very reproducible and in good agreement with the certified values (Table 2.3). One field blank was analysed every 10 samples. Most target compounds were not detected in blanks, or were detected at levels equivalent to a concentration in dust of below 1 ng/g, except BDE-209, which was detected in blanks at around 20 ng/g. Even for BDE-209, concentrations in blanks were always less than 5 % of the concentrations detected in samples. Concentrations of each compound found in blanks are listed in Table 2.3. The limits of detection for each target compound are defined by a 3:1 signal to noise ratio, assuming a notional sample mass of 50 mg, and listed in Table 2.4.

Table 2.3: Measured concentrations of target compounds in SRM and field blank for UK dust samples, ng/g

Compound	Reference value[a]	SRM (n=3) this study	Blank (n=6)
BDE-28	46.9±4.4	48.7±1.9	N.D.
BDE-47	497±46	529.3±11.2	0.3±0.2
BDE-99	892±53	821.3±13.1	0.2±0.2

Compound	Reference value[a]	SRM (n=3) this study	Blank (n=6)
BDE-100	145±11	151.2±3.8	0.2±0.2
BDE-153	119±1	121.9±5.6	0.1±0.2
BDE-154	83.5±2.0	104.6±2.3	0.5±0.2
BDE-183	43.5±3.5	44.3±7.3	N.D.
BDE-209	2510±190	2488.0±164.8	23.8±2.3
PBEB	9.0±3.7	6.8±0.8	0.4±0.4
EH-TBB	26-40	41.8±3.2	0.8±1.3
BTBPE	32-62.2	52.9±11.2	1.0±0.9
BEH-TEBP	574-1300	1096.0±62.5	1.7±2.9
DBDPE	N.A[b]	N.D.[c]	N.D.
α-HBCDD	19-25	29.2±10.0	1.1±1.0
β-HBCDD	4.2-5.7	6.2±2.0	0.3±0.2
γ-HBCDD	80-125	181.0±83.5	2.4±2.4

a. reference values of PBDEs are certified value of NIST, for NBFRs and HBCDDs, the reference values are adopted from Abdallah et al. (2008); Ali et al. (2011b); Brown et al. (2014); Sahlstrom et al. (2012) and Van den Eede et al. (2012)
b. not available
c. not detected

Table 2.4: Limits of detection for dust samples, ng/g

Compound	Limit of detection (ng/g)
BDE-28	0.2
BDE-47	0.2
BDE-99	0.2
BDE-100	0.2
BDE-153	0.4
BDE-154	0.4
BDE-183	1.0
BDE-209	2.6
PBEB	0.2
EH-TBB	0.2
BTBPE	1.0
BEH-TEBP	0.2
DBDPE	9.2
α-HBCDD	0.2
β-HBCDD	0.2
γ-HBCDD	0.16

Recoveries were monitored along with every sample to evaluate the data quality (Table

2.5). It can be found that both SRM and blank samples displayed a very good recovery data which lay in a normal range (40 %~110 %) with low fluctuation. However, exceptional high recoveries were found in real samples for some internal standard, especially ^{13}C-BTBPE and ^{13}C-BEH-TEBP. Theoretically, the recovery will not exceed 100 %, and also considering the normal recoveries in SRM and blank samples, and ^{13}C-HBCDDs in real sample, we can infer the "actual" recoveries for PBDEs and NBFRs were still in a normal range, but the "nominal" ones were overestimated for some reason. One possible reason is a matrix effect. Due to a more complicated composition of the samples analysed in this study, there may be some co-eluting chemicals which are absent from the SRM and blank samples which either suppress the signal of the recovery determination standard PCB-129, or interfere with the signal for the internal standard, which may both lead to a higher nominal recoveries of the internal standards. Another reason might be mass axis drift. The mass axis of the mass spectrometer may drift during a run, introducing measurement errors. Considering that PCB-129 has the shortest retention time of our target compounds, subsequent mass axis drift after it has eluted, may explain higher apparent recoveries of later eluting internal standards. Regardless of which of these explanations are the cause of the occasional elevated recoveries, it is important to note that the accuracy of the concentrations of BTBPE and BEH-TEBP will not be affected, as the response of these will be affected proportionally to their ^{13}C analogues used as internal standards. Moreover, interference between internal standard and target compound can be excluded as no extremely high response

of target compound was found in high recovery cases.

Table 2.5: Recoveries (%) of internal standard in SRM, field blank and real UK dust samples

Compound	SRM (n=3)	Blank (n=6)	Real dust sample (n=60)
BDE-77	55±6.3	104±25.8	149±26.3
BDE-128	44±5.5	64±15.8	147±46.4
^{13}C-BTBPE	67±5.3	46±20.4	310±129.9
^{13}C-BEH-TEBP	68±6.5	58±32.1	300±140.9
^{13}C-BDE-209	61±7.2	49±18.9	180±93.5
^{13}C-α-HBCDD	56±26.1	88±26.8	50±30.2
^{13}C-β-HBCDD	86±22.5	78±16.6	58±14.8
^{13}C-γ-HBCDD	69±21.8	61±8.5	59±10.0

2.6.2 International dust

In total, 9 aliquots of SRM2585 (organics in house dust, NIST) and 9 lab blank samples were analysed to evaluate the reliability of the method and recoveries of each sample were calculated to evaluate the reproducibility. Concentration data obtained for SRM analyses were very reproducible and in good agreement with the certified values (Table 2.6). Also, the recoveries were stable and lay in a reasonable range between 30 % and 110 % (Table 2.7). The good performance of SRM samples ensure the reliability of our method. Moreover, background interference can be omitted as most target compounds were not detected in blanks, or were detected at levels equivalent to a concentration in dust of below 1 ng/g (Table 2.6). The only outlier was BDE-209, which was detected in blanks at around 60 ng/g (Table 2.6), considering the high concentration of BDE-209 however, this background was acceptable. To calibrate the result of BDE-209, mean value of blank samples are subtracted from the results of real samples. The high and

stable recoveries for blanks (50 %~110 %, Table 2.7) indicated a low loss of target compounds during the pre-treatment process, thus a reliable result. Recoveries of real samples were good, and performed better than those in 2.6.1 after the improvement of pre-treatment method (Table 2.7).

Table 2.6: Measured concentrations of target compounds in SRM and lab blank for international dust samples, ng/g

Compound	Reference value[a]	SRM (n=9)	Blank (n=9)
BDE-28	46.9±4.4	46.7±4.7	N.D.
BDE-47	497±46	554.8±63.0	1.1±2.0
BDE-99	892±53	933.9±93.0	N.D.
BDE-100	145±11	153.9±19.8	0.1±0.4
BDE-153	119±1	122.6±18.9	0.1±0.2
BDE-154	83.5±2.0	99.1±11.1	0.0±0.1
BDE-183	43.5±3.5	51.1±8.6	N.D.
BDE-209	2510±190	2724.9±476.2	62.7±14.3
PBEB	9.0±3.7	6.3±0.6	N.D.
EH-TBB	26-40	34.1±7.6	0.2±0.5
BTBPE	32-62.2	35.4±5.7	N.D.
BEH-TEBP	574-1300	1085.7±76.7	N.D.
DBDPE	N.A[b]	N.D.[c]	N.D.
α-HBCDD	19-25	36.3±11.4	1.0±1.4
β-HBCDD	4.2-5.7	9.3±3.0	0.0±0.1
γ-HBCDD	80-125	105.5±43.5	0.3±0.7

a. reference values of PBDEs are certified value of NIST, for NBFRs and HBCDDs, the reference values are adopted from Abdallah et al. (2008); Ali et al. (2011b); Brown et al. (2014); Sahlstrom et al. (2012) and Van den Eede et al. (2012)
b. not available
c. not detected

Table 2.7: Recoveries (%) of internal standard in SRM, lab blank and real international dust samples

Compound	SRM (n=9)	Blank (n=9)	Real dust samples (n=116)
BDE-77	72±9.7	68±12.9	109±25.0
BDE-128	69±11.2	66±28.1	97±33.3
^{13}C-BTBPE	90±32.3	67±35.2	190±92.8
^{13}C-BEH-TEBP	81±15.2	68±51.2	165±107.6
^{13}C-BDE-209	107±12.0	51±19.2	102±52.2
^{13}C-α-HBCDD	33±7.3	93±22.0	47±22.3
^{13}C-β-HBCDD	43±8.4	63±7.2	45±22.8
^{13}C-γ-HBCDD	44±8.4	64±5.2	41±20.2

2.6.3 Kitchen utensils

Recoveries were calculated along with each sample to monitor the data quality with Table 2.8 showing that all recoveries lay in a normal range. The high standard deviation of ^{13}C-BTBPE and ^{13}C-BEH-TEBP recovery was caused by extremely high recovery (300%~400%) of one sample, which means the overall data quality is still reliable.

Table 2.8: Recoveries (%) of internal standard in kitchen utensil samples (n=30)

Compound	Recovery
BDE-77	123±37.8
BDE-128	115±37.7
^{13}C-BTBPE	129±83.7
^{13}C-BEH-TEBP	105±61.1
^{13}C-BDE-209	107±47.6

2.6.4 Oil transfer experiment

To evaluate the reliability of analytical method for oil and to calibrate background interference, 3 blank oil samples were analysed along with experimental samples. Satisfactory results were obtained with recoveries ranging from 60 %~130 % (Table

2.9) and all compounds not detected, except BDE-209 (Table 2.10). Concentrations of BDE-209 were corrected by subtracting the mean value of blank samples from experimental samples.

Table 2.9: Recoveries (%) of internal standard in blank oil samples (n=3)

Compound	Recovery
BDE-77	124±15.6
BDE-128	117±28.0
^{13}C-BTBPE	118±26.2
^{13}C-BEH-TEBP	62±10.0
^{13}C-BDE-209	101±28.4

Table 2.10: Measured concentrations of target compounds in blank oil samples (n=3), ng/mL

Compound	concentration
BDE-28	<0.02
BDE-47	<0.02
BDE-99	<0.02
BDE-100	<0.02
BDE-153	<0.04
BDE-154	<0.04
BDE-183	<0.1
BDE-209	5.5±0.4
PBEB	<0.02
EH-TBB	<0.02
BTBPE	<0.1
BEH-TEBP	<0.02
DBDPE	<0.9

To evaluate the loss during the cooking experiment, a matrix spike test experiment was conducted 5 times by spiking a known amount of all target compounds and internal standards into blank oil samples before the cooking experiment. The matrix spike "test samples" were then analysed and recoveries of all compounds calculated (Table 2.11).

Recoveries of all compounds showed good performance ranging around 100%, and recoveries of target compound showed consistent deviation with coordinating internal standard recoveries (Table 2.11), ensuring precise quantification.

Table 2.11: Recoveries (%) of internal standard and target compound in matrix spike oil samples (n=5)

	Recovery	Target compound/IS ratio
BDE-77 (IS)	135±10	
BDE-28	128±9	95±3
PBEB	99±6	73±3
BDE-47	113±8	84±1
BDE-100	130±5	96±5
BDE-99	173±13	128±8
EH-TBB	252±42	187±31
BDE-128 (IS)	147±23	
BDE-154	129±10	89±9
BDE-153	137±14	94±6
BDE-183	125±16	85±2
^{13}C-BTBPE (IS)	177±27	
BTBPE	170±24	96±2
^{13}C-BEH-TEBP (IS)	78±9	
BEH-TEBP	68±10	87±3
^{13}C-BDE-209 (IS)	133±16	
BDE-209	133±18	101±1
DBDPE	138±18	104±16

Recoveries of cooking transfer experiment oil samples were calculated to evaluate data quality and good results were obtained (Table 2.12).

Table 2.12: Recoveries (%) of internal standard in cooking experiment oil samples (n=30)

Compound	Recovery
BDE-77	121±26.5
BDE-128	128±32.3
^{13}C-BTBPE	162±80.3
^{13}C-BEH-TEBP	75±32.6
^{13}C-BDE-209	131±64.5

2.7 Statistical analysis

Statistical analysis of the data was conducted using Microsoft Excel 2013 to generate descriptive statistics, with all other statistical procedures conducted using IBM SPSS Statistics 19.0. In all instances, where concentrations were below the detection limit, the concentration was assumed to equal half of the detection limit.

Chapter 3 Concentrations of BFRs in matched samples of UK kitchen and living room dust

This chapter contains material taken verbatim from Kuang, J., Ma, Y., Harrad, S., 2016. Concentrations of "legacy" and novel brominated flame retardants in matched samples of UK kitchen and living room/bedroom dust. Chemosphere 149, 224-230.

3.1 Synopsis

Compared with great concerns raised on BFRs in indoor dust, no studies on BFRs in kitchen dust exist, which is a surprising omission, given that people may spend a substantial proportion of time in this microenvironment, and that kitchens contain a substantial number of goods such as microwave ovens, dishwashers, food processors, fridges, and freezers that because their plastic components represent a fuel source in the event of fire, are likely to be flame-retarded. In addition, the restriction of PBDEs and HBCDDs makes contamination of NBFRs an emerging issue. To report for the first time BFR concentrations in kitchen dust and test the hypothesis that BFR concentration in kitchen dust will be higher in other rooms of the same house, we collected kitchen-living room paired dust samples from 30 UK houses and analysed concentrations of 8 PBDEs (BDE-28, 47, 99, 100, 153, 154, 183 and 209), 5 NBFRs (PBEB, EH-TBB, BTBPE, BEH-TEBP and DBDPE) and α-, β-, γ-HBCDDs in dust. Moreover, to test the hypothesis that restriction on PBDEs will lead to a decrease on PBDE concentration and increase on NBFR concentration, we compared our results with a previous UK

study based on samples from the same region. BDE-209 was found to be the most abundant (22–170,000 ng/g) BFR among all target ones, followed by γ-HBCDD (1.7–21,000 ng/g), α-HBCDD (5.2–4,900 ng/g), β-HBCDD (2.3–1,600 ng/g), BDE-99 (2.6-1,440 ng/g), BDE-47 (0.4–940 ng/g), DBDPE (nd-680 ng/g) and BEH-TEBP (2.7-630 ng/g). The concentrations in kitchens and living rooms/bedrooms are moderate compared with previous studies. Concentrations of BDE-209 in living room/bedroom dust were significantly lower and those of DBDPE significantly higher ($p<0.05$) compared to concentrations recorded in UK house dust in 2006 and 2007. This may reflect changes in UK usage of these BFRs. All target BFRs were present at higher concentrations in living rooms/bedrooms than kitchens. With the exception of BDE-28, PBEB and DBDPE, these differences were significant ($p<0.05$). No specific source was found that could account for the higher concentrations in living rooms/bedrooms. Wipe samples of 14 kitchen appliances from 4 investigated kitchens were collected and analysed via LC-HRMS for the presence of FRs not targeted in our initial analyses. These analyses revealed the presence of TBBPA and some PFRs, which may partly explain the lower target BFR concentrations in kitchen dust than in living room/bedroom dust.

3.2 Concentrations of BFRs

Table 3.1 lists minimum, maximum, and median concentrations of target BFRs in both kitchen and living room/bedroom dust in this study, while a boxplot (Figure 3.1) illustrates the concentration range and profile of target BFRs in our samples. Based on

concentration range, the 16 BFRs targeted in this study may be categorised into three groups. BDE-28, PBEB, BDE-100, EH-TBB, BDE-154, BDE-153, BDE-183 and BTBPE belong to the first group, ranging from not detected to several tens ng/g with median concentrations lower than 10 ng/g. The second group contains BDE-47, BDE-99, BEH-TEBP, DBDPE and α-, β-, γ-HBCDDs, for which median concentrations range from 10 ng/g to hundreds ng/g and concentrations range from several ng/g to in excess of 1,000 ng/g. Finally, group 3 consists of BDE-209 only, for which concentrations range from several tens ng/g to more than 100,000 ng/g with a median value of nearly 1,000 ng/g. The concentration ranges and profiles obtained in this study are broadly consistent with previous studies as shown in Figure 3.2. This Figure plots median concentration values for exemplar previous studies (Abdallah et al., 2008; Ali et al., 2013; Ali et al., 2012a; Ali et al., 2011a; Ali et al., 2012b; Allen et al., 2013; Bjorklund et al., 2012a; Brown et al., 2014; Carignan et al., 2013; Coakley et al., 2013; Dirtu et al., 2012; Dodson et al., 2012; Harrad and Abdallah, 2011; Harrad et al., 2008; Kalachova et al., 2012; Kang et al., 2011; Kefeni and Okonkwo, 2012; Nguyen Minh et al., 2013; Ni and Zeng, 2013; Shoeib et al., 2012; Stasinska et al., 2013; Tang et al., 2013; Thuresson et al., 2012; Vorkamp et al., 2011; Whitehead et al., 2013; Yu et al., 2012), alongside those detected in kitchen and living room/bedroom dust in this study (represented as red and black dots respectively). It can be seen that for most compounds, concentrations in this study are lower than previously reported, especially for BDEs-47, -154 and -153. This finding is not inconsistent with a reduction in the use of the

Penta-BDE formulation since the early-mid-2000s. In contrast, concentrations of NBFRs, HBCDDs and BDE-209 recorded in this study are similar or even slightly higher than previously reported, which is consistent with the later introduction (or absence to date) of restrictions on use of these BFRs.

Table 3.1: Maximum (max), minimum (min) and median values of kitchen dust BFR concentration (K, ng/g), living room/bedroom dust BFR concentration (L, ng/g) and matched kitchen-living room/bedroom dust BFR concentration ratio (K/L)

Compound	K			L			K/L		
	max	min	median	max	min	median	max	min	median
BDE-28	150	<0.2	1.2	55	<0.2	1.0	9.55	0.10	1.00
BDE-47	940	0.4	7.6	590	2.4	13	10.30	0.05	0.54
BDE-99	1,400	2.6	17	930	4.0	33	15.37	0.06	0.46
BDE-100	320	<0.2	1.7	140	0.7	3.2	7.23	0.03	0.40
BDE-153	410	0.1	1.7	170	<0.4	1.9	10.02	0.01	0.58
BDE-154	180	<0.4	0.4	60	<0.4	0.7	8.64	0.03	0.52
BDE-183	29	<1.0	1.9	120	0.6	4.2	4.57	0.02	0.46
BDE-209	32,000	22	590	170,000	170	1,500	3.92	0.03	0.33
PBEB	25	<0.2	0.3	15	<0.2	0.4	4.45	0.06	0.84
EH-TBB	290	<0.2	4.1	450	<0.2	12	2.85	0.01	0.37
BTBPE	10	<1.0	1.2	97	<1.0	4.5	5.29	0.02	0.44
BEH-TEBP	420	2.7	36	630	7.8	75	2.35	0.05	0.36
DBDPE	450	<9.2	74	680	21	120	12.09	0.03	0.72
α-HBCDD	3,800	5.2	110	4,900	75	280	2.88	0.05	0.37
β-HBCDD	1,100	2.3	29	1,600	6.4	67	1.86	0.08	0.41
γ-HBCDD	13,000	1.7	35	21,000	14	110	34.85	0.003	0.37

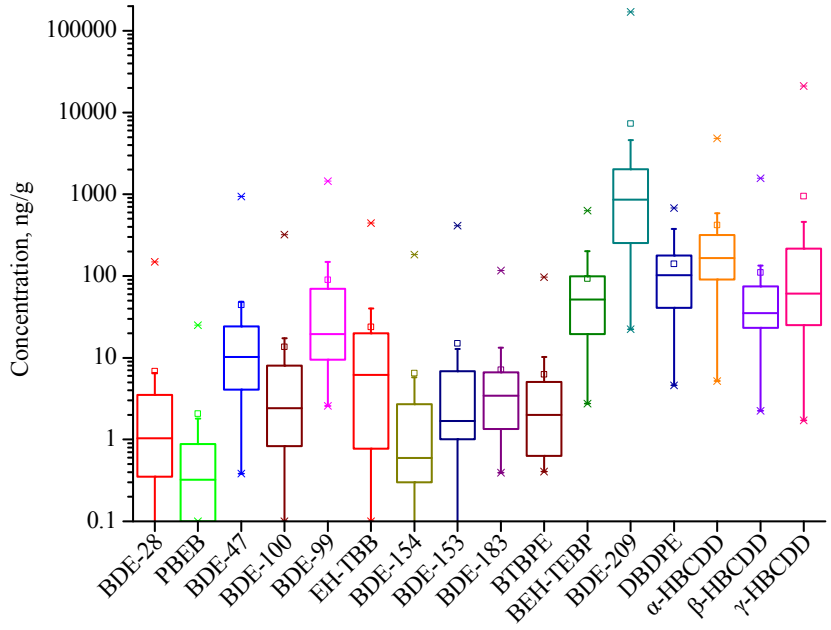


Figure 3.1: Concentration range of BFRs in this study

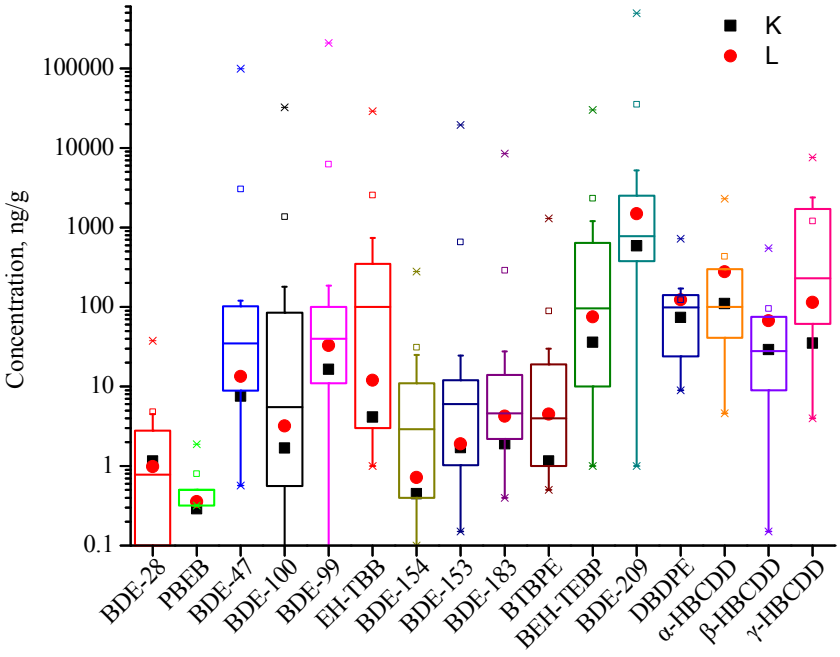


Figure 3.2: Median concentrations of target BFRs in this study (K, kitchen; L, living room/bedroom) compared to the range of medians reported in selected previous studies

3.3 Is there evidence of temporal changes in BFR concentrations in living room/bedroom dust following restrictions on PBDE use?

To investigate the impact of recent restrictions on manufacture and use of PBDEs on concentrations of PBDEs and potential replacement NBFRs in UK indoor dust, we compared concentrations of individual PBDEs, BTBPE, and DBDPE in living room and bedroom dust in our study, with those reported for 30 UK living room dust samples collected between 2006 and 2007 (Harrad et al., 2008). Before doing so, we first conducted a t-test comparison of log-transformed concentrations of our target BFRs in our living room and bedroom dust samples to verify the validity of aggregating these data in this context. This revealed no significant differences ($p>0.05$) between concentrations in living room and bedroom dust for any of our target BFRs. Consequently, we compared BFR concentrations in living room dust from 2006-07 with our combined data for living room and bedroom dust via a t test comparison of log-transformed concentrations in the two temporally-distinct sample groups. This revealed concentrations of most target BFRs to be statistically indistinguishable ($p>0.05$) between the two time periods. However, concentrations of BDE-209 and BDE-154 are significantly lower ($p<0.05$) and those of DBDPE and BDE-28 significantly higher ($p<0.05$) in this (later) study. While it is hard to rationalise the opposite trends in BDEs-28 and -154, and acknowledging the small sample numbers involved; the apparent decrease in concentrations of BDE-209, coupled with the corresponding increase of DBDPE, is not inconsistent with the 2008 introduction of restrictions on use of Deca-

BDE in the EU (European Court of Justice, 2008), and reports that DBDPE is the main alternative to Deca-BDE (Covaci et al., 2011).

3.4 Are concentrations of BFRs higher in kitchen than living room/bedroom dust?

To test our hypothesis that concentrations of BFRs in kitchen dust will exceed significantly those in living area and bedroom dust from the same homes, we conducted a paired t test comparison between concentrations of individual BFRs in kitchen dust and those in living room and bedroom dust. This revealed concentrations for all but BDE-28, PBEB, and DBDPE to be significantly higher ($p<0.05$) in living room and bedroom dust compared to that from kitchens. Moreover, although not significant ($p>0.05$), a higher concentration was still observed for BDE-28, PBEB and DBDPE in living room/bedroom dust compared to kitchen dust. The higher concentrations observed in living rooms and bedrooms compared to the corresponding kitchens are not attributable simply to the respective number of putative sources in the two microenvironments. Kitchens in this study contained more potential sources, such as: fridges, microwave oven, washing machines, ovens, toasters, and curtains etc. than living rooms/bedrooms (which contained mainly carpets, TVs, computers, sofas, and curtains). Considering that carpet was absent from all the kitchens in this study, while being the most frequently reported putative source in living rooms/bedrooms (present in 21/30 of these microenvironments), we examined further whether the presence/absence of carpets in this study could explain the differences between kitchens

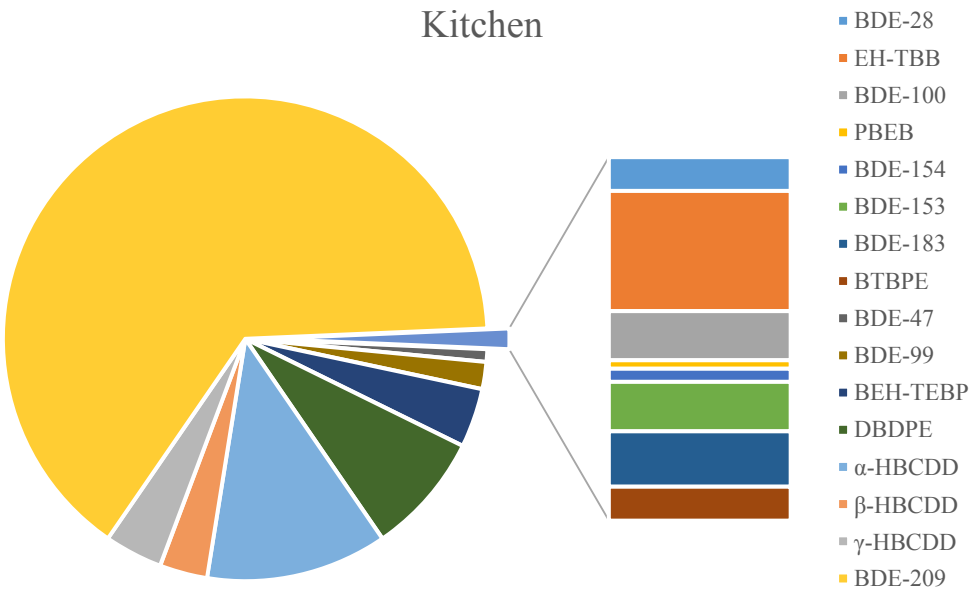
and living rooms/bedrooms. To do so, we classified the 60 dust samples into 3 groups: i.e. kitchen samples (K), bare floor living room/bedroom samples (BL) and carpeted living room/bedroom samples (CL) and subjected data on BFR concentrations (in this instance not log-transformed) in samples in each of these groups to a Kruskal-Wallis test. However, the mean ranks of BL and CL are very close (Table 3.2) and both are much higher than those of kitchen samples for most compounds. This result indicates that the presence of carpet does not significantly influence the concentrations of our target BFRs in living room/bedroom dust. Hence, the absence of carpet from kitchens does not account for the lower concentrations compared to living rooms/bedrooms.

Table 3.2: Mean ranks of BFR concentration in carpeted living room/bedroom (CL), bare floor living room/bedroom (BL) and kitchen (K) of Kruskal-Wallis test

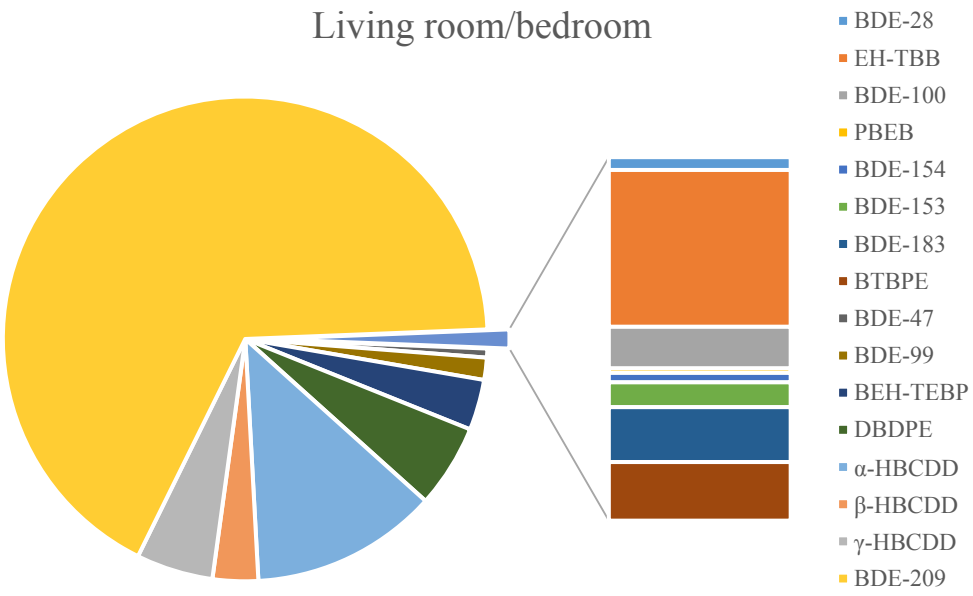
Compound	CL	BL	K
BDE-28	29.93	27.75	29.68
PBEB	30.45	33.38	27.83
BDE-100	35.83	34.88	23.85
EH-TBB	35.58	33.25	24.45
BDE-154	34.65	31.31	25.58
BDE-153	34.03	31.06	26.07
BDE-183	35.33	25.38	24.05
BTBPE	35.70	35.75	23.70
BDE-47	35.88	33.63	24.15
BDE-99	34.38	35.19	24.73
BEH-TEBP	37.67	33.25	23.05
DBDPE	34.20	28.75	26.57
α-HBCDD	36.80	34.94	23.18
β-HBCDD	36.33	37.44	22.83
γ-HBCDD	33.67	31.31	26.23
BDE-209	34.95	34.31	24.58

In summary, this study reveals no evidence that the presence of carpet can explain the

significantly elevated BFR concentrations in living room/bedroom dust compared to kitchen dust. We therefore investigated the reasons driving this difference further, by comparing the BFR profile in these two microenvironment categories. Figure 3.3 is drawn based on the median value of each compound from which it can be found that the composition profiles of kitchen and living room/bedroom dust are similar. To further confirm this, we carried out a Wilcoxon test to compare the mass percentage of each compound in living room/bedroom and kitchen dust. To minimise the overwhelming impact of dominant components such as BDE-209, all target compounds were classified into three groups according to their concentration level as described in section 2.1. At the group level, the relative abundance of groups 1, 2, and BDE-209 were not significantly different between kitchen and living room/bedroom dust. Next, the percentage of each compound was calculated based on the total concentration of the group to which it was assigned. This approach revealed a significantly higher proportion ($p=0.001$) of BDE-28 in kitchens but higher proportions of BTBPE ($p=0.022$) and α-HBCDD ($p=0.035$) in living rooms/bedrooms. The proportion of β-HBCDD was also lower in kitchens, but at a significance level of $p= 0.056$. However, no significant difference was observed for γ-HBCDD ($p=0.600$). Notwithstanding these differences in the relative abundances of a small number of our target BFRs, there appears no clear evidence of major differences between the BFR profiles in kitchens and living rooms/bedrooms, which suggests that there are no major differences in source types between these two microenvironment categories.



(a)



(b)

Figure 3.3: Median BFR compositions in dust from kitchens (a) and living rooms/bedrooms (b)

Another reason which may explain the higher BFR concentrations in living rooms than

in kitchens is that FRs applied in kitchen appliances might differ to those applied in products present in living rooms, and might not therefore be included in the 16 BFRs measured. To test this hypothesis, we collected surface wipe samples from kitchen electrical appliances from 4 of the kitchens from which dust was collected. A high resolution LC-MS-MS (UPLC-Orbitrap-HRMS) was applied in non-target screening mode to analyse wipe samples, in an effort to identify FRs not measured by our targeted GC-MS methods.

To focus our screening efforts, a hand held XRF was used to measure Br content in kitchen devices, with wipe samples collected from appliances containing >100 ppm Br. As described in 2.1.4, a clinical bactericidal wipe soaked with 70 % w/w isopropyl alcohol was used to wipe the surface of the device. Table 3.3 shows the results of our XRF screening, revealing that Br was widely detected in kitchen appliances, sometimes at an extremely high concentration (W2), implying of the presence of BFRs.

Table 3.3: Br content in kitchen appliances

Appliance	Wipe sample #	Br content, ppm
Kitchen 1		
Fridge 1	W1	157 ± 45
Fridge 2		N.D.
Microwave oven 1	W2	$(110.8 \pm 3) \times 10^3$
Microwave oven 2	W3	1900 ± 44
Washing machine	W4	221 ± 34
Rice cooker 1		30 ± 6
Rice cooker 2		N.D.
Rice cooker 3		N.D.
Stove	W5	129 ± 44
Boiler		N.D.

Appliance	Wipe sample #	Br content, ppm
Fume		N.D.
Kitchen 2		
Kettle		N.D.
Washing machine	W6	875 ± 72
Microwave oven	W7	379 ± 10
Rice cooker		N.D.
Fridge	W8	87 ± 36
Fume		N.D.
Stove		N.D.
Kitchen 3		
Microwave oven		N.D.
Stove	W9	269 ± 46
Washing machine	W10	581 ± 58
Rice cooker		N.D.
Kettle		N.D.
Fridge	W11	224 ± 38
Kitchen 4		
Microwave oven		67 ± 18
Washing machine	W12	711 ± 65
Stove	W13	240 ± 45
Rice cooker 1		N.D.
Rice cooker 2		N.D.
Rice cooker 3		N.D.
Rice cooker 4		N.D.
Fridge 1	W14	157 ± 32
Fridge 2		N.D.
Kettle		N.D.
Toaster		N.D.

Thanks to the high resolution of the orbitrap mass spectrometer, we were able to identify BFRs using the accurate mass to charge ratio (m/z) values of chromatographic peaks. Besides those PBDEs, HBCDDs and 5 NBFRs already quantified in dust samples, the occurrence of more BFRs was evaluated in 14 surface wipe samples. The additional BFRs screened are: TBBPA, hexachlorocyclopentadienyldibromo-cyclooctane (HCDBCO), octabromo-1,3,3-trimethyl-1-phenylindane (OBIND), 2,4,6-

tribromophenyl allyl ether (ATE), 2-bromoallyl 2,3,6-tribromophenylether (BATE), 2, 3-dibromopropyl-2, 4, 6-tribromophenyl ether (DPTE), hexabromobenzene (HBB) and PBB. However, as shown in Table 3.4, only a few BFRs were detected in a small number of samples. W2, that displayed the highest Br content, also contained the widest range of BFRs (TBBPA, EH-TBB, ATE and BTBPE). Overall, TBBPA was the most frequently detected BFR, found in 3 out of 14 samples. The low detection frequency of BFRs in wipe samples will likely be at least partly due to the high detection limit of our surface wipe screening method. However, the high detection frequency of TBBPA under the existed analytical method reminded us an omission in our previous target analysis, and supported our hypothesis that BFRs applied in kitchen appliances might not be included in our target compounds.

Table 3.4: BFRs detected in wipe samples

Sample#	BDE-183	TBBPA	EH-TBB	ATE	BTBPE	Br content, ppm
W2		√	√	√	√	110 K, rank 1
W3		√			√	1900, rank 2
W5		√				130, rank 13
W12	√					700, rank 4

An alternative explanation of the relatively low Br and BFR concentrations in kitchen appliances and associated product surface wipes is that an important group of FRs (PFRs) may be present in kitchen appliances to impart flame retardancy. We therefore screened for PFRs in the surface wipe samples. Mainstream PFRs including tris(2-chloroethyl) phosphate (TCEP), tris(1,3-dichloroisopropyl) phosphate (TDCIPP), tris(2-chloroisopropyl) phosphate (TCIPP), triethyl phosphate (TEP), Tris(nonylphenyl)

phosphate (TnPP), tri-n-butyl-phosphate (TnBP), tri-iso-butyl phosphate (TiBP), tris-(butoxyethyl)-phosphate (TBEP), triphenyl phosphate (TPhP), tricresylphosphate (TCP), and 2-ethylhexyl diphenyl phosphate (EHDPP) were screened for, with six detected in wipe samples (Table 3.5). This presence of PFRs in kitchen appliance surface wipes and by inference in the kitchen appliances may help account for the relatively low Br concentrations detected.

Table 3.5: PFRs detected in wipe samples

Sample#	TnPP	TCIPP	TCEP	TBEP	TPhP	EHDPP
W1		√	√	√	√	√
W2		√	√	√	√	√
W3		√	√	√	√	√
W4		√	√	√	√	√
W5		√	√	√	√	
W6	√	√		√	√	
W7		√		√	√	
W8	√	√	√	√	√	
W9		√			√	
W10		√		√	√	
W11	√	√		√	√	
W12	√	√	√	√	√	
W13		√	√	√	√	
W14	√	√		√	√	

In addition to the likelihood (supported by the results of our kitchen appliance surface wipe screening above) that BFRs additional to those targeted in our kitchen and living room dust samples have been applied to impart flame retardancy to kitchen appliances; a generally higher BFR emission rate in living rooms/bedrooms may also responsible for the higher BFR concentrations in dust from living rooms/bedrooms compared to those in kitchen dust. Although kitchens contain more putative sources, the rate at

which BFRs may be emitted from these are influenced by factors such as material, volume and BFR content of sources, which can combine to obscure clear relationships between BFR contamination of dust and putative source counts. Another potential contributory factor may be that given the greater use of water for cleaning and cooking in kitchens, it is reasonable to assume that kitchens are more humid than living rooms/bedrooms. This may lead to greater water content on the surface of kitchen dust that may impede the sorption of BFRs from air.

3.5 Conclusions

Concentrations of 16 BFRs in dust from living rooms/bedrooms and kitchens from 30 UK homes are moderate compared with previous studies. Comparison of data for living rooms/bedrooms in this study with previous data for living room dust from the same region of the UK in 2006-07, reveals concentrations of BDE-209 to have fallen significantly, while concentrations of DBDPE have risen. Concentrations of 13 out of our 16 target BFRs in kitchen dust are exceeded significantly by those in living room/bedroom dust. Comparison of BFR patterns in both microenvironment categories suggests that the sources of our target BFRs are similar in both. The higher concentrations in living rooms/bedrooms may be due to a combination of factors such as: kitchen appliances contain FRs different to those in living rooms/bedrooms and that are targeted in this study, an overall higher emission intensity of our target BFRs in living rooms and bedrooms, and a lower uptake of BFRs by dust in kitchens due to the higher humidity.

Chapter 4 BFRs in black plastic kitchen utensils: Concentrations and human exposure implications

This chapter contains material taken verbatim from Kuang, J., Abdallah, M.A.-E., Harrad, S., 2017. Brominated flame retardants in black plastic kitchen utensils: Concentrations and human exposure implications. Science of the Total Environment. (Accepted)

4.1 Synopsis

Waste electrical and electronic equipment (WEEE) may be dismantled to recover precious metals and plastics, with the plastics recovered being recycled. However, use of recycled plastics containing BFRs in new materials has led to concerns that restricted BFRs may be present in newly manufactured goods, including those which are not subject to flame retardancy regulations such as kitchen utensils. Considering the close contact with food and human skin of kitchen utensils, BFR contaminated utensils may pose a potential exposure and health risk. To investigate the extent to which kitchen utensils are contaminated with BFRs and the potential for resultant human exposure, we collected 96 plastic kitchen utensils and screened for Br content using a hand-held X-ray fluorescence (XRF) spectrometer. Only 3 out of 27 utensils purchased after 2011 contained detectable concentrations of Br ($\geq$ 3 μg/g). In contrast, Br was detected in 31 out of the 69 utensils purchased before 2011. Eighteen utensils with Br content higher than 100 μg/g, and 12 new utensils were selected for GC-MS analysis of BFRs. BFRs

targeted were PBDEs BDE-28, 47, 99, 100, 153, 154, 183 and 209, and NBFRs PBEB, EH-TBB, BTBPE, BEH-TEBP and DBDPE. The ability of XRF to act as a surrogate metric of BFR concentration was indicated by a significant (Spearman coefficient = 0.493; p=0.006) positive relationship between Br and ΣBFR concentration. Measurements of ΣBFRs were always exceeded by those of Br. This may be due partly to the presence of BFRs not targeted in our study and also to reduced extraction efficiency of BFRs from utensils. Of our target BFRs, BDE-209 was the most abundant one in most samples, but an extremely high concentration (1,000 μg/g) of BTBPE was found in one utensil. Simulated cooking experiments were conducted to investigate BFR transfer from selected utensils (n=10) to hot cooking oil, with considerable transfer (20 % on average) observed. Estimated median exposure via cooking with BFR contaminated utensils was 60 ng/day for total BFRs, with BDE-209 accounted for 50 ng/day. In contrast, estimated exposure via dermal contact with BFR-containing kitchen utensils was less substantial.

4.2 Bromine content of kitchen utensils

Table 4.1 reports Br concentrations in the utensil samples analysed using hand-held XRF. Of the 96 samples analysed, 69 were reported by the donors to be 5 years or older, 6 were aged 2 years, while 21 were purchased for this study between December 2015 and July 2016. It should be noted that “age” in this study refers only to the donor-reported date of purchase to the nearest year. It is important to note not only the uncertainty associated with such self-reported data, but that the date of purchase does

not equate to the date of manufacture but to the date of availability on the market. Notwithstanding this, for convenience, we use “age” as an abbreviation of “date of availability on the market” from herein. Table 4.1 also lists the utensil type, with the main categories being: spoons (n=33), spatulas (n=18) and ladles (n=12). Of the 27 utensils aged < 5 years, only 1 (3.7 %) contained >100 μg Br/g, 2 (7.4 %) contained ~ 5 μg Br/g, with the remaining 24 (88.9 %) containing <3 μg Br/g. In contrast, for utensils aged ≥5 years, 17 (24.6 %) contained > 100 μg Br/g, 13 (18.9 %) contained between 5 and 100 μg Br/g, and 34 (49.3 %) containing <3 μg Br/g. Given this apparent dichotomy between “older” and “newer” utensils, we evaluated the significance of this using non-parametric statistical tests as our data did not display a normal distribution. We first conducted a Mann-Whitney rank test to compare Br concentrations between the two age groups. This revealed Br concentrations to be significantly greater in utensils ≥5 years old (p=0.016). This was consistent with a Spearman correlation analysis which showed utensil age and Br content to be significantly and positively correlated (r=0.237, p=0.020).

Table 4.1: Bromine Concentrations (μg/g) in Kitchen Utensils

Sample #[a]	Utensil type	Br content, μg/g	Date of purchase[b]	Age, years
P1	Solid spoon	<3	2015	New
P2	Thermos cup lid	<3	2015	New
P3	Thermos cup lid	180	2015	New
P4	Thermos cup lid	<3	2015	New
P5	Thermos cup lid	<3	2015	New
P6	Food package	<3	2015	New
P7	Food package	<3	2015	New
P8	Food package	<3	2015	New

Sample #[a]	Utensil type	Br content, µg/g	Date of purchase[b]	Age, years
P9	Food package	<3	2015	New
P10	Ladle	350	2008	8
P11	slotted spatula	300	2008	8
P12	spaghetti server	<3	2013	2
P13	Solid spatula	<3	2013	2
P14	solid spatula	<3	2013	2
P15	Food clip	<3	2013	2
P16	slotted spoon	100	2009	7
P17	Solid spoon	600	2009	7
P18	Solid Spoon	6,000	2006	10
P19	solid spoon (grip)	200	Before 2011	>5
P20	Ladle	120	2001	15
P21	slotted spatula	400	2001	15
P22	solid spoon (grip)	150	2006	10
P23	Masher	90	2009	7
P24	solid spoon (grip)	170	2006	10
P25	slotted spoon (grip)	150	2006	10
P26	Ladle (grip)	140	2006	10
P27	slotted spoon	100	2009	7
P28	slotted spoon (grip)	170	2002	14
P29	Scissors	130	2002	14
P30	Scissors	4,000	2002	14
	slotted spatula	<3	2009	7
	Solid spatula	<3	2009	7
	Ladle	<3	2009	7
	slotted spatula	<3	2009	7
	slotted spoon	40	Before 2011	>5
	Solid Spoon	<3	2007	9
	slotted spoon	<3	2001	15
	Solid Spoon	<3	2016	New
	Ladle	<3	2016	New
	slotted spatula	<3	2016	New
	Solid spoon	30	2009	7
	Solid spoon	<3	2009	7
	Masher	<3	2008	8
	slotted spatula	50	2008	8
	slotted spatula	<3	2008	8
	spaghetti server	<3	2008	8
	Solid spoon	<3	2008	8
	Ladle	<3	2008	8

Sample #[a]	Utensil type	Br content, µg/g	Date of purchase[b]	Age, years
	slotted spoon	85	2006	10
	skimming spoon	<3	2006	10
	Masher	<3	2006	10
	Not recorded	<3	2006	10
	Not recorded	<3	2006	10
	Not recorded	<3	2006	10
	Not recorded	<3	2006	10
	Not recorded	<3	2006	10
	Cut board	10	2009	7
	Spatula	20	2009	7
	Ladle	<3	2009	7
	Solid spoon	<3	2006	New
	slotted spatula	<3	1996	20
	Solid spoon	<3	1996	20
	Ladle	<3	1996	20
	slotted spoon	20	1996	20
	Masher	<3	1996	20
	Spatula	<3	1998	18
	dotted spoon	<3	1998	18
	Masher	<3	1998	18
	Spatula	10	2002	14
	Masher	<3	2002	14
	Scissors	60	2002	14
	Whisk	<3	2014	2
	Masher	<3	2014	2
	spaghetti server	10	2001	15
	slotted spatula	<3	2001	15
	Ladle	<3	2001	15
	slotted spoon	<3	2001	15
	Masher	30	2001	15
	solid spoon	<3	2016	New
	slotted spatula	<3	2016	New
	Masher	<3	2016	New
	Ladle	5	2016	New
	slotted spoon	<3	2016	New
	slotted spoon	<3	2016	New
	slotted spoon	7	2016	New
	Scissors	<3	2016	New
	solid spoon	<3	2011	5
	slotted spatula	<3	2011	5

Sample #[a]	Utensil type	Br content, µg/g	Date of purchase[b]	Age, years
	Ladle	<3	2011	5
	Ladle	8	2011	5
	Fork	<3	2011	5
	Spatula	<3	Before 2011	>5
	Solid spoon	50	Before 2011	>5
	Solid spoon	<3	Before 2011	>5
	Slotted spoon	60	Before 2011	>5
	Skimming spoon	<3	Before 2011	>5

[a]Sample # refers to sample analysed for BFR content – see Table 4.2. Samples not assigned a number were not analysed for their BFR content
[b]Owner's estimate of purchase date

4.3 BFR concentrations in kitchen utensils

Based on the Br concentration data, those utensils containing >100 µg Br/g (n=18) were subjected to GC-MS determination of their BFR content, together with 12 utensils containing <100 µg Br/g to provide context. These 30 samples are numbered 1~30 in Table 4.1.

Table 4.2 shows that utensils with high Br content (>100 µg/g) display a higher BFR concentration than those indicated by XRF to contain <100 µg/g Br. We tested the statistical significance of this relationship using non-parametric tests as our data did not display a normal distribution. Specifically, a Mann-Whitney rank test showed the difference to be statistically significant ($p=0.007$), with the positive relationship between Br and BFR concentrations confirmed by Spearman correlation analysis ($r=0.493$, $p=0.006$). However, more detailed inspection of Table 4.2 reveals there is substantial discrepancy between our BFR and Br data for the same samples. To be

explicit, our ΣBFR measurements are always lower than the corresponding Br measurements – and in some cases substantially so, for example, sample 18 contained 6,000 μg Br/g, but displayed a ΣBFR concentration of 0.6 μg/g. This is most likely due to some compounds not included in our list of target BFRs for example TBBPA, and/or low extraction efficiency for BFRs using our method.

We first tested the hypothesis that the discrepancy between Br and ΣBFR was because the former was due to the presence of one or more BFRs not targeted by our GC-MS analyses. To do so, we studied sample 18 in more detail. Tentative support for this explanation is supplied by the observation of several unidentified peaks on the m/z 79 and 81 traces in the GC mass chromatogram for sample 18. Hence, following solvent exchange from iso-octane to methanol we re-analysed this sample on a LC-high resolution MS system (UPLC-Orbitrap-MS, Thermo Fisher Scientific, Bremen, Germany) in an attempt to identify BFRs not quantified via our GC-MS method such as TBBPA or HBCDD. However, this did not provide an obvious explanation for the discrepancy, and thus incomplete extraction efficiency can not be ruled out as a cause in this instance at least. To avoid dissolving the plastic during BFR extraction and thus expedite more rapid analysis, a low polarity aliphatic solvent (hexane) was chosen for extraction. We note that other studies have used different solvents (Allen et al. (2008), Aldrian et al. (2015) used toluene, and Gallen et al. (2014) used dichloromethane), and thus our BFR measurements may be underestimates of the true value. Also, as TBBPA

is a reactive BFR which binds more firmly with polymers than additive BFRs like PBDEs, hexane may be less effective at extracting it from polymers, leading it to be not detected even in our LC-high resolution MS screening.

Table 4.2: BFR concentrations in kitchen utensils, ng/g

Sample #	BDE-28	PBEB	BDE-47	BDE-100	BDE-99	EH-TBB	BDE-154	BDE-153	BDE-183	BTBPE	BEH-TEBP	BDE-209	DBDPE	ΣBFRs, µg/g	Br, µg/g
P1	<0.2	0.2	6.3	7.0	42	<0.2	7.8	16	36	530	<0.2	1,100	72	1.8	<3
P2	<0.2	<0.2	37.4	6.9	26	<0.2	1.3	2.7	14	78	<0.2	620	16	0.8	<3
P3	<0.2	<0.2	110	36	150	<0.2	12	22	100	1,200	<0.2	2,500	23	4.1	180
P4	<0.2	<0.2	0.5	<0.2	1.4	<0.2	0.4	1.1	16	3.8	27	260	<9.2	0.3	<3
P5	<0.2	<0.2	1.2	0.3	2.3	<0.2	<0.4	0.5	3.9	5.4	<0.2	37	<9.2	0.1	<3
P6	<0.2	0.2	<0.2	0.5	4.6	0.5	<0.4	0.7	<1.0	<1.0	150	14	12	0.2	<3
P7	<0.2	<0.2	<0.2	<0.2	1.3	<0.2	<0.4	<0.4	<1.0	<1.0	<0.2	<2.6	<9.2	<0.01	<3
P8	<0.2	<0.2	<0.2	<0.2	1.1	<0.2	<0.4	<0.4	<1.0	<1.0	<0.2	<2.6	<9.2	<0.01	<3
P9	<0.2	<0.2	<0.2	<0.2	0.7	<0.2	<0.4	1.1	4.4	8.4	<0.2	340	290	0.6	<3
P10	130	<0.2	360	68	330	<0.2	48	90	330	1,400	<0.2	17,000	<9.2	20	350
P11	100	<0.2	210	82	93	<0.2	4.6	21	36	60	<0.2	2,200	<9.2	2.8	300
P12	<0.2	<0.2	7.4	1.3	7.7	<0.2	0.9	1.8	14	<1.0	<0.2	1,300	<9.2	1.4	<3
P13	0.6	<0.2	25	4.8	30	<0.2	2.9	6.2	34	1.1	<0.2	2,500	<9.2	2.6	<3
P14	<0.2	<0.2	11	4.1	21	<0.2	3.6	5.6	24	<1.0	<0.2	1,200	<9.2	1.3	<3
P15	<0.2	<0.2	38	9.9	49	<0.2	5.4	9.1	46	<1.0	<0.2	2,100	<9.2	2.3	<3
P16	<0.2	<0.2	9.5	<0.2	10	<0.2	8.9	36	27	<1.0	6.8	660	58	0.8	100
P17	<0.2	<0.2	36	34	180	<0.2	1,000	1,800	1,600	<1.0	<0.2	1,000	340	6.0	600
P18	<0.2	1.1	15	82	100	<0.2	21	14	23	210	<0.2	140	<9.2	0.6	6,000
P19	<0.2	<0.2	8.8	1.8	10	<0.2	1.3	2.3	8.8	<1.0	350	260	110	0.8	200
P20	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	<0.4	<1.0	<1.0	<0.2	81	<9.2	0.1	120
P21	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	<0.4	<1.0	<1.0	17	220	<9.2	0.2	400

Sample #	BDE-28	PBEB	BDE-47	BDE-100	BDE-99	EH-TBB	BDE-154	BDE-153	BDE-183	BTBPE	BEH-TEBP	BDE-209	DBDPE	ΣBFRs, µg/g	Br, µg/g
P22	<0.2	4.0	57	30	240	<0.2	15	25	130	<1.0	46	110,000	5,500	120	150
P23	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	<0.4	<1.0	<1.0	<0.2	78	<9.2	0.1	90
P24	120	11	1,000	110	530	900	40	170	139	280	30,000	8,100	5,200	47	170
P25	79	14	1,000	110	370	950	23	110	66	180	25,000	1,900	3,700	34	150
P26	15	8.4	970	43	130	830	5.2	29	49	200	22,000	2,700	7,200	34	140
P27	<0.2	<0.2	<0.2	<0.2	9.0	<0.2	3.7	14	45	35	10	2,500	280	2.9	100
P28	64	8.3	82	30	260	<0.2	30	560	1,100	1,500	140	81,000	5,700	90	170
P29	<0.2	<0.2	10	0.2	12	<0.2	7.6	1,600	180	18,000	5.7	3,200	420	23	130
P30	<0.2	33	<0.2	<0.2	12	<0.2	210	120,000	13,000	1,100,000	<0.2	140,000	1,900	1,400	4,000

Given our observation that Br concentrations were significantly higher in samples ≥5 years old, than in younger utensils, we examined our data for similar age-related differences in ΣBFR concentrations, again using non-parametric tests in accordance with the distribution of our data. A Mann-Whitney rank test found significantly ($p=0.014$) higher ΣBFR concentrations in utensils ≥5 years old than in those <5 years in age. This was consistent with Spearman correlation analysis ($r=0.501$, $p=0.005$) that showed a positive relationship between BFR concentration and utensil age. These findings are likely attributable to two main factors: (1) the introduction in restrictions in use of PBDEs in the mid-2000s onwards, and (2) the more recent introduction of restrictions on the recycling of BFR-treated plastics.

In terms of the BFR distribution pattern, BDE-209 was the most abundant BFR detected and in 17 out of 30 samples (56.7 %), BDE-209 accounted for more than 70 % of ΣBFR. This is consistent with the fact that BDE-209 is mainly used in hard plastics like polyamide (Arias, 2001 cited by Alaee et al., 2003) which is used widely in kitchen utensils. Aside of this general predominance of BDE-209 however, the BFR pattern varied widely between individual utensils. For example, while P22, P23 and P24, which came from the same donor and were purchased at the same time, all contained a high percentage of BEH-TEBP (65 % ~ 75 % ΣBFR); P10 and P11 (donated by the same individual and purchased at the same time) contained substantial contributions of less brominated PBDEs like BDE-47 and -99; while P29 and P30 (which were the two

handles of the same pair of scissors) were dominated (~80 % ΣBFR) by BTBPE. These 3 examples indicate that as well as age, production batch may be an important additional factor influencing the Br and BFR concentration and pattern.

4.4 BFR transfer from utensil to oil in simulated cooking process

Table 4.3, as well as Figures 4.1 and 4.2 show the transfer of individual BFRs and ΣBFR from the aliquots of utensils subjected to the simulated cooking experiments. The percentage transfer in Figure 4.1 and 4.2 was calculated as $r = m_{BFR-oil} / (c_{BFR-plastic} \times m_{plastic}) \times 100\%$, where $m_{BFR-oil}$ is the mass of BFR extracted by oil, measured by GC-MS, $c_{BFR-plastic}$ is BFR concentration in plastic utensils and $m_{plastic}$ is mass of plastic used in cooking experiment. Transfer was substantial for all compounds, especially during the 1st cooking exposure (batch 1), ranging from 20 % to 100 %. The extent of transfer decreased in the order batch 1>batch 2>batch 3 and with increasing degree of bromination for PBDEs. In particular, while BDE-209 was abundant in most utensils, its transfer to oil was negligible in 6 of 10 cases. However, for samples P22, P24, P28 and P30 that contained BDE-209 concentrations in the range 10~100 μg/g, more substantial transfer was observed. The generally lower transfer efficiency of BDE-209 in our experiments is likely due to a combination of lower solubility in oil of BDE-209 compared to other BFRs, alongside greater binding of BDE-209 to plastic.

In some cases, the transfer exceeded 100 %. This may be attributable to a number of

factors, namely: (a) inhomogeneous distribution of BFRs in the kitchen utensils which could result in the BFR content of the aliquot of the utensil subjected to cooking differing from that in the aliquot used to determine BFR concentration; and (b) that hot oil may be a more effective solvent for extracting BFRs from kitchen utensils than hexane.

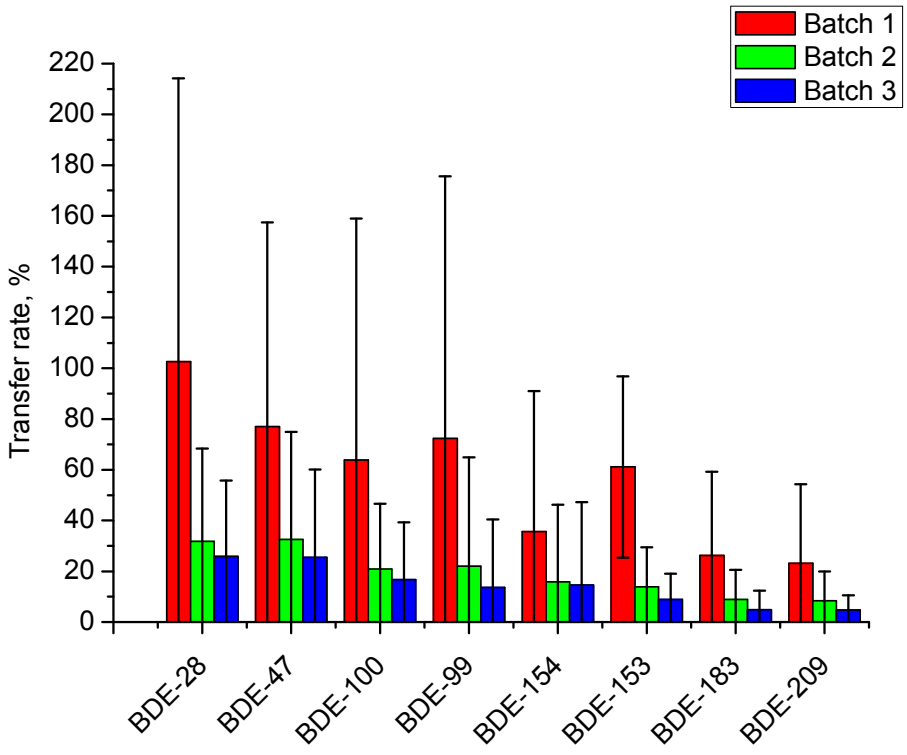


Figure 4.1: Average percentage transfer of PBDEs from kitchen utensils in simulated cooking experiments (y-error bar represents σ_{n-1})

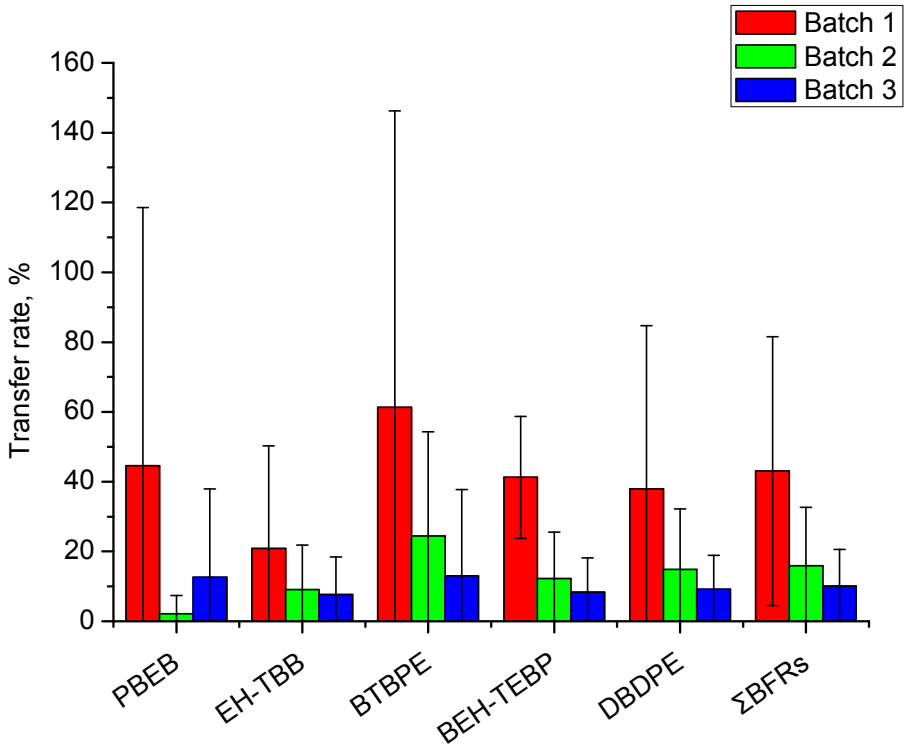


Figure 4.2: Average percentage transfer of NBFRs and ΣBFRs from kitchen utensils in simulated cooking experiments (y-error bar represents σ_{n-1})

Table 4.3: BFR transfer from kitchen utensils (ng BFR/g plastic[a]) in simulated cooking experiments

Sample	BDE-28	PBEB	BDE-47	BDE-100	BDE-99	EH-TBB	BDE-154	BDE-153	BDE-183	BTBPE	BEH-TEBP	BDE-209	DBDPE	ΣBFRs
P1	<0.2	0.2	6.3	7.0	42	<0.2	7.8	16	36	530	<0.2	1,100	72	1,800
Batch1	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	14	<1.0	100	<0.2	62	<9.2	170
Batch2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	<0.4	<1.0	<1.0	<0.2	<2.6	<9.2	<16
Batch3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	<0.4	<1.0	<1.0	<0.2	<2.6	<9.2	<16
P3	<0.2	<0.2	110	35.6	150	<0.2	12	22	100	1,200	<0.2	2,500	23	4,100
Batch1	<0.2	<0.2	<0.2	<0.2	13	<0.2	<0.4	7.4	<1.0	<1.0	<0.2	<2.6	<9.2	21
Batch2	<0.2	<0.2	5.8	<0.2	0.3	<0.2	<0.4	<0.4	<1.0	<1.0	<0.2	11	<9.2	17
Batch3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	<0.4	<1.0	<1.0	<0.2	<2.6	<9.2	<16
P10	130	<0.2	360	68	330	<0.2	48	90	330	1,400	<0.2	17,000	<9.2	20,000
Batch1	270	2.0	410	170	170	<0.2	<0.4	21	<1.0	92	<0.2	4.8	<9.2	1,100
Batch2	86	1.2	110	41	41	<0.2	<0.4	5.2	<1.0	<1.0	<0.2	3.6	<9.2	290
Batch3	68	1.3	85	26	30	<0.2	<0.4	4.0	<1.0	20	<0.2	10	<9.2	250
P11	100	<0.2	210	81	93	<0.2	4.6	21	36	60	<0.2	2,200	<9.2	2,800
Batch1	200	2.3	320	140	160	<0.2	<0.4	21	<1.0	150	0.6	4.6	<9.2	1,000
Batch2	63	0.5	57	14	21	<0.2	<0.4	2.3	<1.0	35	<0.2	<2.6	<9.2	190
Batch3	53	0.9	33	6.1	12	<0.2	<0.4	<0.4	<1.0	<1.0	<0.2	<2.6	<9.2	100
P17	<0.2	<0.2	36	34	180	<0.2	1,000	1,800	1,600	<1.0	<0.2	990	250	6,000
Batch1	<0.2	<0.2	12	<0.2	59	<0.2	210	560	1,300	<1.0	<0.2	41	<9.2	2,200
Batch2	<0.2	<0.2	4.9	14	16	<0.2	54	140	310	I[b]	<0.2	5.0	<9.2	740
Batch3	<0.2	<0.2	3.5	21	19	<0.2	86	180	330	I[b]	<0.2	<2.6	<9.2	920
P18	<0.2	1.1	15	82	100	<0.2	21	14	23	210	<0.2	140	<9.2	600

Sample	BDE-28	PBEB	BDE-47	BDE-100	BDE-99	EH-TBB	BDE-154	BDE-153	BDE-183	BTBPE	BEH-TEBP	BDE-209	DBDPE	ΣBFRs
Batch1	<0.2	2.3	36	140	340	<0.2	38	13	<1.0	100	<0.2	8.4	<9.2	670
Batch2	<0.2	<0.2	19	52	140	<0.2	20	4.8	<1.0	52	<0.2	<2.6	<9.2	290
Batch3	<0.2	<0.2	12	33	91	<0.2	22	4.3	<1.0	30	<0.2	2.7	<9.2	200
P22	<0.2	4.0	57	30	249	<0.2	15	25	130	<1.0	46	110,000	5,500	120,000
Batch1	<0.2	<0.2	11	<0.2	130	<0.2	4.1	610	59	270	17	100,000	6,400	110,000
Batch2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	240	21	390	<0.2	34,000	1,900	36,000
Batch3	<0.2	0.4	5.7	<0.2	<0.2	<0.2	<0.4	94	<1.0	390	<0.2	16,000	1,200	18,000
P24	120	11	1,000	110	530	900	40	170	130	280	30,000	8,100	5,200	47,000
Batch1	<0.2	4.9	990	55	230	370	15	61	43	220	7,800	3,400	3,300	17,000
Batch2	<0.2	<0.2	810	29	78	160	4.5	16	10	220	3,100	1,000	1,200	6,700
Batch3	<0.2	<0.2	920	22	53	140	2.9	7.9	5.3	200	1,800	570	820	4,600
P28	64	8.3	82	30	260	<0.2	30	560	1,100	1, 500	140	81,000	5,700	90,000
Batch1	7.7	3.3	34	<0.2	77	4.5	16	620	870	1,100	82	48,000	4,300	55,000
Batch2	<0.2	<0.2	9.8	<0.2	53	<0.2	9.4	260	380	430	36	21,000	2,200	25,000
Batch3	<0.2	5.7	<0.2	<0.2	14	<0.2	2.7	100	150	170	26	10,000	1,100	12,000
P30	<0.2	33	<0.2	<0.2	12	<0.2	210	120,000	13,000	1,100,000	<0.2	140,000	1,900	1,400,000
Batch1	<0.2	7.2	<0.2	<0.2	0.2	<0.2	66	39,000	2,900	100,000	<0.2	32,000	220	180,000
Batch2	<0.2	4.6	<0.2	<0.2	<0.2	<0.2	25	12,000	1,200	56,000	<0.2	15,000	120	85,000
Batch3	<0.2	3.0	<0.2	<0.2	<0.2	<0.2	30	13,000	1,200	51,000	<0.2	15,000	140	81,000
Batch4	<0.2	2.7	<0.2	<0.2	<0.2	<0.2	24	7,400	980	40,000	0.2	13,000	120	62,000

[a]Amount of BFRs extracted in oil (Batch 1, 2, 3) is expressed as $m_{BFR\text{-}oil}/m_{plastic}$, i.e. mass of BFR detected in each olive oil extract divided by the mass of plastic tested.

[b]Interference prevented quantification.

4.5 Preliminary exposure assessment

We considered two pathways via which human exposure to BFRs in kitchen utensils may occur: (a) transfer to food when cooking, and (b) transfer through dermal contact. The following are preliminary evaluations of the likely magnitude of human exposure via such pathways.

4.5.1 Exposure via cooking

Exposure via cooking was estimated based on the results of our simulated cooking experiments – note that as some utensils for which BFR concentrations were determined were unlikely to come into contact with hot oil during use (e.g. scissors), these utensils (P2-P5, P6-P9, plus P29 and 30) were excluded from our estimations. To estimate exposure resulting from contact between the utensil and hot oil and subsequent ingestion of the oil we made several assumptions. The first of these are that: 1) over the useful "lifetime" of every 200 mL oil (assumed 1 week) used for deep frying, the utensil is in contact with oil at 160 ^{o}C for a total period over that week of 15 min; and 2) the extent of BFR transfer is proportional to the specific surface area (i.e. surface area per unit utensil volume) of the utensil in contact with oil. We further assumed that the utensil dimensions likely to come into contact with oil during cooking are 10 cm × 8 cm × 2 mm (equivalent to that of a typical spatula), yielding a specific surface area of 10 cm^{-1}. This compares quite closely with the specific surface area of 19 cm^{-1} of the 5 mm × 4 mm × 2 mm plastic cuboids used in our cooking experiments. Based on these

assumptions, we estimated the amount of BFR transferred from kitchen utensils to hot oil during cooking via the equation below.

$$c_{BFR-oil} = \left(c_{BFR-utensil} \times m_{utensil} \times r_{real}\right) / V_{oil} \quad (4\text{-}1)$$

Where:

$c_{BFR-oil}$ is BFR concentration transferred to hot cooking oil (ng/mL);

$c_{BFR-utensil}$ is BFR concentration (ng/g) in kitchen utensils coming into contact with hot oil;

$m_{utensil}$ is mass of utensil contact with hot oil when cooking, whose size is 10 cm × 8 cm × 2 mm, and for density, a value of 1.4 g/cm^3 was applied based on the average measured value for several utensils on this study. So $m_{utensil} = V_{utensil} \times \rho_{utensil}$ = 10 cm × 8 cm × 2 mm ×1.4 g/cm^3 = 22.4 g;

r_{real} is BFR transfer rate (unitless) in real-life scenario and is calculated based on transfer rate obtained in cooking experiment (r_{exp}), specific surface area of utensil in experiment (A_{exp}) and in real-life scenario (A_{real}):

$$r_{real} = \frac{A_{real}}{A_{exp}} \times r_{exp} = \frac{10\ \text{cm}^{-1}}{19\ \text{cm}^{-1}} \times r_{exp} = 0.53 r_{exp};$$

V_{oil} is volume of oil involved in cooking which is assumed to be 200 mL.

Thus,

$$c_{BFR-oil} = \frac{c_{BFR-utensil} \times 22.4\ \text{g} \times 0.53 r_{exp}}{200\text{mL}} = 0.059 c_{BFR-utensil} r_{exp}\ \text{ng/mL} \quad (4\text{-}2)$$

According to 2015-2020 dietary guidelines for Americans (US DHHS and DA, 2015), the recommended daily oil intake for an adult is 27 g. We assume that deep fried oil accounts for 15 % of daily oil intake on average, and that as noted on the food information label of the oil used, the density of olive oil was 0.9 g/mL; thus the daily BFR exposure amount is:

$$\begin{aligned} E_{BFR-oil} &= 15\% \times c_{BFR-oil} \times \frac{27 \text{ g/day}}{0.9 \text{ g/mL}} \\ &= 15\% \times 0.059 c_{BFR-utensil} r_{exp} \frac{\text{ng}}{\text{mL}} \times \frac{27 \text{ g/day}}{0.9 \text{ g/mL}} \\ &= 0.27 c_{BFR-utensil} r_{exp} \text{ ng/day} \end{aligned} \quad (4\text{-}3)$$

Here we use median and maximum concentration of the 20 utensils (P1, P10~P28) as the value of $c_{BFR-utensil}$ for median and high exposure scenario estimates, and the mean transfer rate of the 3 batches in the cooking experiments is used for the value of r_{exp}. The resultant exposure estimates are shown in Table 4.4.

Table 4.4: BFR exposure (ng/day) via cooking in median and high exposure scenarios[a]

	BDE-28	PBEB	BDE-47	BDE-100	BDE-99	EH-TBB	BDE-154	BDE-153	BDE-183	BTBPE	BEH-TEBP	BDE-209	DBDPE	ΣBFRs
r_{exp}	53.4%	19.8%	45.0%	37.6%	40.0%	12.5%	22.3%	27.9%	13.2%	32.9%	20.6%	11.7%	20.7%	-
Median	NA[b]	NA[b]	2.4	0.8	4.4	NA[b]	0.3	1.1	1.3	0.1	NA[b]	52.2	1.7	64.2
High	18.7	0.7	125.2	10.3	51.0	31.6	58.2	135.7	55.9	130.6	1,651.4	3,545.0	393.0	6,207.3

[a]low exposure scenario was not calculated because minimum concentrations of all BFRs but BDE-209 were not detected; median and high exposure scenarios assume transfer from a utensil containing the median and maximum values of $c_{BFR-utensil}$ respectively;

[b]not available due to a not detected concentration.

As shown in Table 4.4, daily exposure to total BFRs are ~60 ng and ~6,000 ng under median and high scenarios, respectively; while those for ΣBDEs are ~60 ng and 4,000 ng respectively. To place these exposure estimates into context, Besis and Samara (2012) reviewed daily intake of PBDEs via different exposure pathways in different countries, and found that dust ingestion could amount to up to 400 ng/day intake in the US and the UK. Intake in other countries was lower, ranging from 50 to 200 ng/day. Dietary intake, as another important exposure pathway, ranged from 50 to 75 ng/day according to Besis's review. Harrad et al. (2004) investigated concentrations of tetra-hexa BDEs in UK duplicate diet samples and estimated dietary exposure of 90 ng/day for ΣPBDEs (tetra- to hexa-BDEs only). D'Silva et al. (2006) investigated concentrations of 17 PBDEs in typical UK diet composite samples in 2003, and the daily dietary exposure for tri- to hepta-BDEs and BDE-209 were estimated to be 80 ng/day and 270 ng/day, respectively. For NBFRs, Tao et al. (2017) detected several NBFRs including EH-TBB, BEH-TEBP, BTBPE, DBPDE and tetrabromoethylcyclohexane (DBE-DBCH) in UK food samples, estimating the average total daily dietary exposure to the sum of these NBFRs for adults was 90 ng/day. This compares with the median and high-end estimates in this study of ~2 and ~2,000 ng/day. To place our exposure estimates into context against non-dietary exposure, Harrad et al. (2008) estimated indoor dust ingestion of PBDEs, DBDPE and BTBPE, and the median exposure for UK adult was about 200 ng/day. Ni et al. (2013) estimated PBDE exposure via indoor dust ingestion in different cities of China, the median exposure for adult ranged from 20 to 100 ng/day.

Compared with estimates of exposure via other pathways from by previous studies, exposure via cooking using BFR-containing utensils is not negligible. Moreover, although the transfer rate of BDE-209 during cooking is not high, it still accounts for the largest proportion (80 %) of exposure via cooking due to its high concentration in utensils.

It is important to emphasise the preliminary nature of our assessment of dietary exposure arising from using BFR-containing utensils. Our simulated cooking experiments involved deep frying, which is likely a worst-case scenario with respect to BFR extraction. Moreover, our estimate of oil-utensil contact occurring for 15 minutes over 1 week is subject to considerable uncertainty and will vary considerably between households, along with the frequency with which individuals will consume deep-fried food. Finally, we focused only on those utensils displaying elevated BFR concentrations, with our high-end exposure estimates based on the most contaminated utensil; thus our high-end estimates are likely a worst-case scenario, with our median estimates more representative of exposure at the population level. Balanced against this, it is not unreasonable to assume that utensils will have contained higher BFR concentrations when new and thus greater BFR transfer will have occurred earlier in the life of some of the older utensils studied here. On the whole therefore, we consider our estimates a reasonable first-level evaluation, and that they provide evidence to suggest that further investigation of the potential for human exposure arising from use of such utensils is

warranted.

4.5.2 Dermal exposure

Considering the high BFR concentration not only in the main body but also in the grip of kitchen utensils, exposure via dermal contact is of concern. Dermal uptake is a complex process involving two major steps. First, the transfer of BFRs from the plastic polymer to the skin surface film liquid (i.e. becomes bioaccessible). Second, the penetration of the skin barrier to reach the blood circulation (i.e. becomes bioavailable) (Abdallah et al., 2015a, c; Pawar et al., 2017). With the exception of HBCDDs (Pawar et al., 2017), an extensive survey of the literature revealed no available data on the dermal bioaccessibility of BFRs. For the second process, Abdallah et al. (2015a) reported on the dermal uptake rates of mono to deca BDEs over a 24 h exposure period. Therefore, our exposure model adopts a conservative approach with the assumption of 100 % bioaccessibility of PBDEs (*in the absence of relevant data*), and data from Abdallah et al. (2015a) were applied for estimation of bioavailability. Daily exposure (ng/day) via dermal contact was calculated by the equation below.

$$\boldsymbol{E = C \times SA \times F \times EF} \quad (4\text{-}4)$$

where E is daily dermal exposure (ng/day), C is the concentration of BFRs in the utensil (ng/cm^2), SA is the skin surface area exposed (cm^2), F is the fraction absorbed by the skin (unitless), EF is the fraction of time in contact with the item (day^{-1}).

To transfer BFR concentration in ng/g to concentration per surface area, a 0.5 mm

depth (h) plastic from the surface of the utensil was assumed. For utensil density ($\rho_{utensil}$) a value of 1.4 g/cm^3 was applied as indicated in section 4.5.1. So

$C\ (area) = h \times \rho_{utensil} \times C\ (mass) = 0.05\ \text{cm} \times 1.4\ \text{g/cm}^3 \times C\ (mass) = 0.07\ C\ (mass)$.

For the exposure area, we used data from the US EPA exposure factors handbook (US EPA, 2011) stating the average surface area of an adult hand is 1070 cm^2 for male and 890 cm^2 for a female. The average area of a single palm was estimated as 1/2 × 1/2 × (1070+890)/2 cm^2 = 245 cm^2. Considering that not the whole palm will contact with kitchen utensils upon handling, a 75 % coefficient was assumed resulting in an exposed skin area (SA) of 184 cm^2. Finally, parameters F and EF were obtained from Abdallah et al. (2015a), who measured various absorbed fraction of PBDEs at different exposure times from 15 min to 24 h.

Over a daily contact time of 15 min, no dermal uptake was observed for any PBDEs which is consistent with the “lag time” reported by Abdallah et al. (2015a) for the studied compounds. Lag time is defined as the time required by a specific chemical from its initial contact with the skin surface to reach the systemic circulation. Low dermal uptake was observed when the contact time was prolonged to 0.5 h and 1 h, except for higher brominated BDEs (Table 4.5).

Table 4.5: PBDE exposure (ng/day) via dermal contact in median and high scenarios[a]

	BDE-28	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	BDE-209	ΣPBDEs
F (0.5 h)[b]	0.07%	0.04%	-[c]	-	-	-	-	-	
Median	NA[d]	0.05	-	-	-	-	-	-	0.05
High	1.19	5.41	-	-	-	-	-	-	6.60
F (1 h)	0.20%	0.13%	0.08%	0.08%	0.03%	0.03%	-	-	
Median	NA	0.17	0.03	0.17	0.02	0.04	-	-	0.43
High	3.40	17.58	1.18	5.51	3.85	456.43	-	-	487.95

[a]exposure in low scenario was not calculated because minimum concentrations of all BFRs but BDE-209 were not detected; median and high exposure scenarios were calculated based on median and maximum BFR concentration of P1~P30;
[b]data obtained from Abdallah et al. (2015a);
[c]no transfer observed;
[d]not available due to a not detected concentration.

Our results indicate that human uptake of PBDEs via dermal contact with cooking utensils is much lower than our intake estimates based on cooking and other pathways (section 4.5.1). The exception to this is for BDE-153 in the 1 h contact high-end scenario, due to the extremely high BDE-153 concentration in scissor sample P30. This could be attributed to the limited daily contact time with utensils, and low penetration efficiency into skin, especially for BDE-209 whose concentration was the highest. Therefore, our findings suggest when using BFR-contaminated kitchen utensils, exposure is dominated by utensil-oil transfer, rather than utensil-skin transfer.

4.6 Conclusions

- 34 % of plastic kitchen utensils analysed in this study contained measurable concentrations of Br.
- Under our extraction procedure, BDE-209 was predominant among our target

BFRs in most utensils, but the pattern of other BFRs varied substantially between utensils. Elevated concentrations of BTBPE and BDE-153 were found in some utensils.

- BFR transfer from utensils into hot oil during simulated cooking experiments was considerable, and differed between BFRs and utensils. Transfer efficiency decreased with increasing Br substitution of PBDEs.
- Using BFR containing utensils for frying may lead to considerable dietary exposure, whilst exposure via dermal contact is less substantial due to limited contact time and barrier effect of skin.

Chapter 5 Concentrations of BFRs in living room dust from Europe, North America and Jordan

5.1 Synopsis

Previous studies have revealed difference on BFR concentrations and distribution patterns among countries. However, most previous studies focus only on samples in 1 country and when comparing results of different studies, different sampling strategies and analysis methods may have an influence on the data. To avoid interference caused by different method, we investigated BFR concentrations in indoor dust across 6 countries using identical sampling (section 2.1.2), clean-up (section 2.4.2) and analytical (section 2.5.1 and 2.5.3) method. Besides, compared with numbers of studies on PBDE concentrations, data on NBFRs are scarce. To gain more knowledge about NBFR occurrence in indoor dust, 5 NBFRs PBEB, EH-TBB, BTBPE, BEH-TEBP and DBDPE were included in our target compounds, together with 8 PBDEs (BDE-28, 47, 99, 100, 153, 154 and 209) and α-, β-, γ-HBCDDs. Briefly, totally 116 living room floor dust samples were collected by vacuum cleaner from Finland (Helsinki, n=20), Greece (Athens, n=10), Spain (Barcelona, n=20), Jordan (Amman, n=19), United States (Houston, n=17) and Mexico (Ciudad Victoria, n=30) and concentrations of BFRs above mentioned were measured in the dust. Similar concentration level and distribution pattern were observed compared with previous studies, with BDE-209, DBDPE, BEH-TEBP and α-,γ-HBCDDs showing the highest concentration ranging

from several tens ng/g to several thousand ng/g, followed by BDE-47, 99 and β-HBCDD ranging from 10 - 100 ng/g. For difference among countries, US showed the highest Penta-BDE concentration, followed by Mexico. Jordan showed a higher Octa-BDE concentration with others. Concentration of Deca-BDE was not significantly different among countries but several extremely high concentrations were observed in Finnish samples. Highest α- and β-HBCDD concentration was observed in Jordan samples while γ-HBCDD showed the highest in Spain. For NBFRs, US and Mexican samples were found to display a similar composition with FireMaster® 550 formulation (EH-TBB:BEH-TEBP=4:1). We estimated exposures of BDE-47, 99, 153 and 209 via dust ingestion, finding them comparable with previous studies, but far below the reference dost set by US EPA.

5.2 Concentration and comparison with previous studies

Table 5.1 summarises the concentrations of each target BFR in dust samples from different countries. The 16 target BFRs can be categorised into several groups according to their concentration ranges. BDE-209, DBPDE, BEH-TEBP and α-,γ-HBCDDs lie in the highest level ranging from several tens ng/g to several thousand ng/g, with median concentrations of several hundred ng/g. BDE-47, 99 and β-HBCDD range from 10 - 100 ng/g mainly, constituting the second group. The third group with the lowest concentrations comprises BDE-28, 100, 153, 154, 183, PBEB, EH-TBB and BTBPE, ranging from not detected (N.D.) to several tens ng/g, with median concentrations of several ng/g. To clearly compare our results with previous studies,

Figure 5.1 shows a box plot of median concentrations of target BFRs from 32 previous studies (Abdallah et al., 2008; Ali et al., 2013; Ali et al., 2012a; Ali et al., 2011a; Ali et al., 2012b; Allen et al., 2013; Besis et al., 2014; Bjorklund et al., 2012a; Carignan et al., 2013; Chow et al., 2015; Civan and Kara, 2016; Coakley et al., 2013; Cristale et al., 2016; Dirtu et al., 2012; Dodson et al., 2012; Harrad and Abdallah, 2011; Harrad et al., 2010; Harrad et al., 2008; Johnson et al., 2010; Kalachova et al., 2012; Kang et al., 2011; Kefeni and Okonkwo, 2012; Kuang et al., 2016; Nguyen Minh et al., 2013; Ni and Zeng, 2013; Shoeib et al., 2012; Stasinska et al., 2013; Tang et al., 2013; Thuresson et al., 2012; Vorkamp et al., 2011; Whitehead et al., 2013; Yu et al., 2012) alongside those from different countries in this study. Figure 5.1 reveals median concentrations in this study to generally lie between the 25th and 75th percentile of previously reported median concentrations for all target BFRs, but with some deviation depending on the country and BFR. For tetra- through hexa-BDEs from BDE-47 to BDE-154, the US samples showed clearly higher median concentrations than those detected in all 5 countries studied here. However, with the exception of the Mexican samples, concentrations in the other countries studied are lower than the median or in some instances the 25th percentile of concentrations reported in previous studies. For BTBPE, BEH-TEBP and DBDPE, most countries investigated in this study show concentrations exceeding the 50th percentile of previous studies, with those of DBDPE exceeding the 75th percentile. In contrast, concentrations reported here for BDE-183, BDE-209 and γ-HBCDD are lower than 50th percentile while median concentrations of BDE-209 for all

6 countries studied here lie between the 25th and 50th percentile of concentrations reported previously.

Table 5.1: Concentrations of target BFRs in each country, ng/g

Country	Statistical Parameter	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	PBEB	EH-EBB	BTBPE	BEH-TEBP	DBDPE	α-HBCDD	β-HBCDD	γ-HBCDD
All countries n= 116	**Average**[a]	1.7	160	310	59	44	29	13	3,300	0.5	330	24	680	1,200	200	34	200
	SD	5.3	450	1,200	220	180	110	52	20,000	1.4	2,100	110	2,800	3,100	310	50	410
	Median	N.D.[b]	18	22	3.0	3.3	2.2	2.0	520	N.D.	7.9	5.3	140	290	100	17	85
	Minimum	N.D.	1.5	2.7	N.D.	N.D.	N.D.	N.D.	38	N.D.	N.D.	N.D.	N.D.	N.D.	9.4	N.D.	N.D.
	Maximum	45	3,500	10,000	2,000	1,700	940	500	200,000	12	23,000	930	27,000	25,000	2,200	340	3,300
Finland n= 20	**Average**	0.1	45	56	12	7.6	5.7	2.2	15,000	0.1	8.3	18	350	1,700	88	17	73
	SD	0.1	85	120	31	19	15	2.7	47,000	0.0	10	46	540	5,400	120	23	140
	Median	N.D.	13	12	1.6	1.5	0.8	0.5	420	N.D.	3.7	4.9	140	340	51	9.9	20
	Minimum	N.D.	2.0	3.8	N.D.	N.D.	N.D.	N.D.	88	N.D.	N.D.	N.D.	N.D.	N.D.	13	0.6	3.4
	Maximum	0.7	350	530	130	82	64	11	**200,000**[c]	0.2	38	210	2,100	**25,000**	560	110	600
Greece n= 10	**Average**	0.1	5.7	8.2	0.8	0.7	0.5	3.6	98	0.1	25	5.7	2,700	220	170	33	120
	SD	0.1	3.8	4.6	0.8	0.6	0.4	6.9	1,100	0.1	73	5.2	8,400	150	140	33	170
	Median	N.D.	4.4	6.8	0.6	0.5	0.4	0.8	600	N.D.	1.2	4.4	61	170	130	27	53
	Minimum	N.D.	**1.5**	**2.7**	N.D.	N.D.	N.D.	N.D.	120	N.D.	N.D.	N.D.	N.D.	78	24	2.2	N.D.
	Maximum	0.4	12	16	2.8	2.1	1.3	22	3,900	0.3	230	19	**27,000**	540	450	110	560
Spain n= 20	**Average**	0.4	19	14	2.2	3.6	1.6	9.4	980	0.4	7.6	5.7	1,100	1,400	200	36	370
	SD	0.8	18	12	2.6	8.1	2.1	35	1,700	0.3	13	7.6	3,000	2,800	210	32	530
	Median	N.D.	11	10	1.6	1.3	0.8	N.D.	380	0.3	4.5	3.6	330	260	140	21	160
	Minimum	N.D.	5.9	4.1	N.D.	N.D.	N.D.	N.D.	130	N.D.	N.D.	N.D.	83	N.D.	16	4.2	35
	Maximum	2.8	81	53	11	36	8.5	160	7,000	1.1	59	26	14,000	12,000	970	140	2,000

Country	Statistical Parameter	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	PBEB	EH-EBB	BTBPE	BEH-TEBP	DBDPE	α-HBCDD	β-HBCDD	γ-HBCDD
Jordan	**Average**	0.5	21	25	4.5	9.4	3.2	40	870	0.2	32	53	370	1,100	540	82	100
n= 19	**SD**	0.5	27	33	6.8	19	3.8	110	770	0.2	110	150	640	2,300	560	85	67
	Median	0.3	11	12	1.9	3.2	1.7	5.0	640	N.D.	4.4	20	150	340	350	50	87
	Minimum	N.D.	3.8	5.0	0.8	0.9	N.D.	N.D.	110	N.D.	N.D.	N.D.	19	35	31	4.6	21
	Maximum	1.7	95	140	26	83	12	**500**	2,600	1	500	680	2,900	10,000	**2,200**	**340**	220
US	**Average**	8.9	720	1,600	300	220	140	24	1,500	2.2	2,000	67	650	750	210	36	130
n= 17	**SD**	9.2	730	1,600	310	239	150	25	1,500	2.2	2,100	70	660	780	210	35	130
	Median	4.3	320	570	94	51	33	9.2	60	1.1	320	7.6	270	270	99	15	77
	Minimum	0.3	21	29	5.1	4.8	3.4	N.D.	**38**	0.2	94	N.D.	110	22	23	3.9	14
	Maximum	**45**	**3,500**	**10,000**	**2,000**	**1,700**	**940**	150	6,700	**12**	**23,000**	**930**	4,300	7,600	1,300	230	570
Mexico	**Average**	1.0	140	240	43	32	22	2.6	690	0.2	140	5.9	160	1,300	86	15	310
n= 30	**SD**	1.6	250	520	93	74	50	3.4	520	0.2	410	7.4	270	2,900	73	14	630
	Median	0.3	30	62	9.8	6.6	4.9	N.D.	540	N.D.	29	3.5	72	360	65	12	110
	Minimum	N.D.	4.4	9.6	0.5	0.5	0.6	N.D.	70	N.D.	0.2	N.D.	16	29	**9.4**	N.D.	6.7
	Maximum	5.6	1,100	2,600	470	380	260	12	2,400	1.3	2,300	28	1,400	14,000	280	66	**3,300**

a: not detected values were treated as half of detection limit when calculating average and standard deviation;

b: not detected;

c: data in bold means the maximum/minimum of the whole data set for all samples studied in this chapter

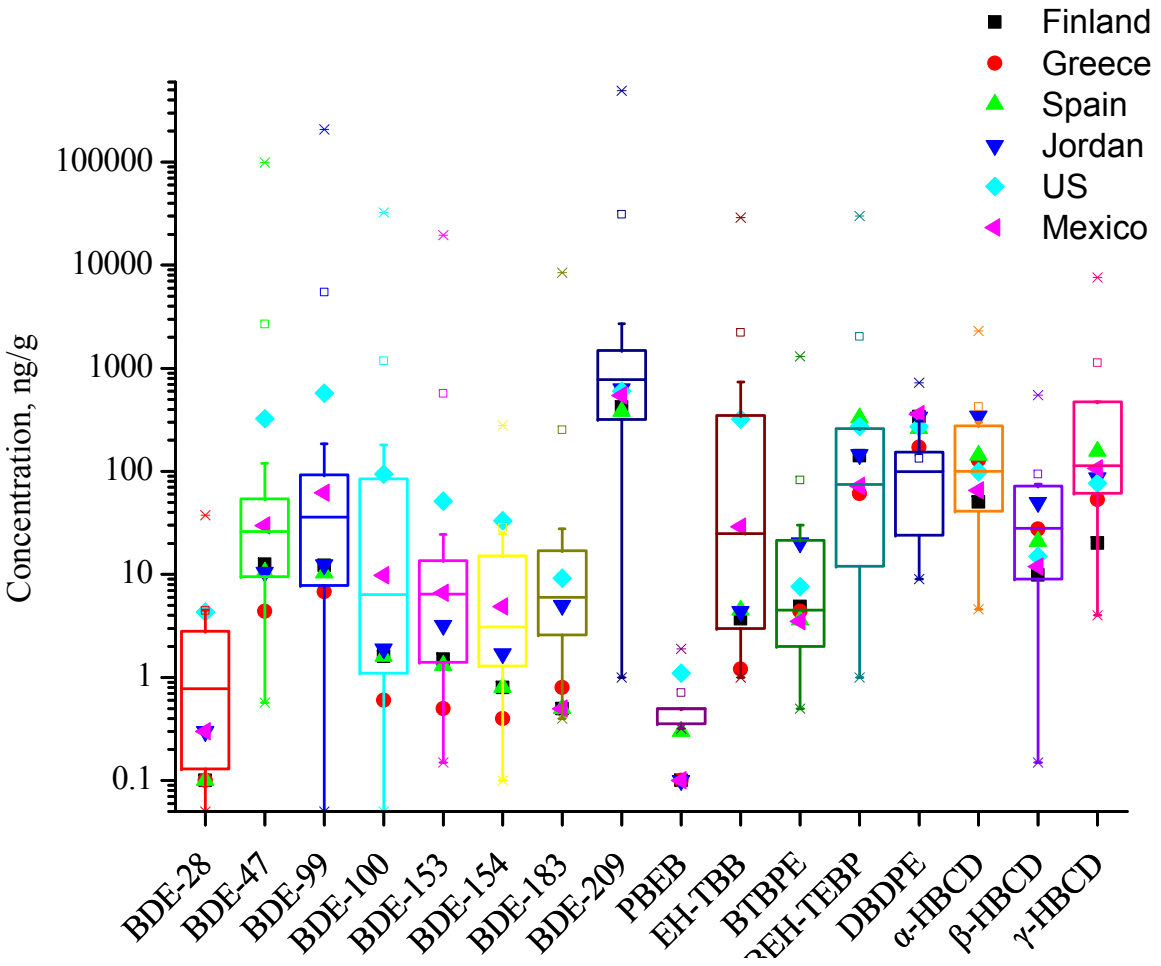


Figure 5.1: Median concentrations (ng/g) of target BFRs in house dust from this study and others

A more detailed comparison with previous studies by country was also conducted. Data from the US are the most abundant and comprehensive, whilst those for the other countries studied here are relatively scarce, or even non-existent. Johnson et al. (2010) reported PBDE concentrations in house dust of Massachusetts, US that concurred closely with those reported in our study with respect to both concentration range and median concentration, with the exception that concentrations of BDE-183 (4-700 ng/g, median 20 ng/g) and BDE-209 (400-30000 ng/g, median 1500 ng/g) were higher in our study. However, other studies about PBDEs in US house dust indicated a 2~5 times higher concentration than those reported here (Watkins, 2011, 2013; Dodson, 2012). Brown et al. (2014) investigated NBFR concentrations in Californian house dust; reporting concentrations of PBEB (<0.64-13 ng/g, median <0.64 ng/g), EH-TBB (<0.64-20,000 ng/g, median 300 ng/g) and BEH-TEBP (<0.64-3,500 ng/g, median 200 ng/g) that are similar to those detected in our US samples, but a lower concentration of DBDPE (<2.6-5,500ng/g, median 80 ng/g) and a higher concentration of BTBPE (<0.64-1,500 ng/g, median 23 ng/g) than reported in this study. In another study of Californian house dust, Dodson et al. (2012) reported concentrations of 4 NBFRs (PBEB not investigated), reporting a similar concentration of BTBPE (3-130 ng/g, median 12 ng/g) and BEH-TEBP (<2-3,800 ng/g, median 260 ng/g) to our study, but a lower concentration of EH-TBB (45-5,900 ng/g, median 100 ng/g) and DBDPE (18-2800 ng/g, median 140 ng/g). For HBCDDs, Abdallah et al. (2008) reported concentrations in Texan office dust to be similar to our data for α-HBCDD (17-1,800

ng/g, median 80 ng/g) and β-HBCDD (6-300 ng/g, median 28 ng/g) but higher than reported here for γ-HBCDD (19-2,000 ng/g, median 300 ng/g). In California, Dodson et al. (2012) reported concentration ranges of 17-910 ng/g, 7-230 ng/g, 13-790 ng/g, and median concentrations of 62 ng/g, 16 ng/g, 73 ng/g for α-, β-, and γ-HBCDDs respectively, which is at the same level with result reported in our study for all HBCDD stereoisomers.

Outside the US, Cristale et al. (2016) reported concentrations in 5 house dust samples from Barcelona, Spain of 8 PBDEs and 4 NBFRs that were also measured in our study. The median concentrations of most compounds in these Spanish samples are lower than those reported this study, with the exception of BDE-183, BDE-209, BTBPE and DBDPE - for example BDE-209 (2,500 ng/g versus 400 ng/g – this study). To our knowledge, concentrations of BFRs in Greek house dust have not previously been reported, although Besis et al. (2014) reported PBDE concentrations in air-conditioner filter dust in Greece (n=20). In that study, although the relative abundance of individual BFRs are similar to this study, absolute concentrations are ~ 2-5 fold higher than reported here, which may probably be caused by the different type of dust (air-conditioner filter dust v.s. floor dust). As reported by Al-Omran and Harrad (2016), BFR concentrations in UK elevated surface dust were significantly higher than in floor dust. The physicochemical properties of air-conditioner filter dust may be more similar with elevated surface dust. Again to our knowledge, previous data on concentrations of

BFRs in house dust from Finland, Jordan and Mexico have not been reported.

5.3 Comparison among countries

5.3.1 Kruskal-Wallis rank test

To compare BFR concentrations among countries, a non-parametric Kruskal-Wallis rank test was conducted for each compound. A non-parametric test rather than a parametric test conducted on log-transformed data was employed as concentrations of BDE-28, BDE-183 and PBEB did not follow a log-normal distribution. The Kruskal-Wallis test showed that with the exception of BDE-209 ($p=0.523$) and DBDPE ($p=0.311$), concentrations of all compounds differed significantly ($p<0.05$) between countries. Our US samples displayed the highest concentrations for tri-hepta BDEs as well as PBEB, EH-TBB (Table 5.2, Figure 5.3~5.9, Figure 5.11, 5.12), and the second highest concentrations of BTBPE and BEH-TEBP (Table 5.2, Figure 5.13, 5.14). Moreover, for those BFRs for which the US samples were the most highly contaminated, the degree of elevation was substantial, except BDE-183 where concentration of Jordan stays close to which of US (Figure 5.9). Interestingly, concentrations of BTBPE and of α- and β-HBCDD were highest in Jordan (Figure 5.13, Figure 5.16, 5.17), while our Spanish dust samples were the most contaminated with BEH-TEBP and γ-HBCDD (Figure 5.14, 5.18), as well as being the second most contaminated for α- and β-HBCDD (Figure 5.16, 5.17). The high HBCDD concentrations in Spanish dust samples is consistent with a higher HBCDD concentrations in Spanish human milk samples

compared with other countries reported by Eljarrat et al. (2009). Also, the predominance of γ-HBCDD (Figure 5.26) in Spanish dust samples was consistent with which in Spanish human milk samples (Eljarrat et al., 2009). Although our Mexican dust samples were not the most contaminated for any of our target BFRs, they displayed the second highest concentrations for 9 moeities, including tri-hexa BDEs, EH-TBB, DBDPE and γ-HBCDD (Table 5.2, Figure 5.3~5.8, Figure 5.12, 5.15, 5.18). The observation that concentrations of tri-hexa BDEs were highest and second highest in the US and Mexico respectively is consistent with the greater consumption of Penta-BDE in North America where >97 % Penta-BDE was used (Alaee et al., 2003). Furthermore, Firemaster® 550, as an important substitute for Penta-BDE, contains EH-TBB and BEH-TEBP in a ratio of approximately 4:1 (Stapleton et al., 2008). To investigate the use of Firemaster® 550, we calculated the EH-TBB:BEH-TEBP ratio for each of our samples, finding that the mean ratios in US and Mexican dust were 2.2 and 0.6, respectively, which is significantly higher (Kruskal-Wallis test, $p<0.05$) than the mean ratio (around 0.1) detected in samples from Europe and Jordan. Moreover, the similarity between the EH-TBB:BEH-TEBP ratio in our US dust samples and that observed in the Firemaster® 550 product suggests widespread use of Firemaster® 550 in US. Likewise, the intermediate values for the Mexican dust samples, suggest substantial use of FM-550 in Mexico.

Table 5.2: Mean rank for each country and significance (sig.) of BFRs in Kruskal-Wallis test

BFR/Country	Finland	Greece	Spain	Jordan	US	Mexico	Sig.
BDE-28	35.30	37.20	45.85	60.47	101.88	63.67	0.000
BDE-47	49.35	17.00	46.40	41.42	100.82	73.33	0.000
BDE-99	47.10	21.90	33.90	44.84	101.65	78.90	0.000
BDE-100	46.45	16.60	36.40	47.26	101.18	78.17	0.000
BDE-153	42.80	19.30	34.45	59.21	99.53	74.37	0.000
BDE-154	41.10	22.10	37.80	52.16	100.76	76.10	0.000
BDE-183	46.83	54.80	46.03	79.71	85.12	47.32	0.000
BDE-209	50.65	61.70	51.05	61.53	69.59	59.43	0.523
PBEB	36.63	51.65	74.43	52.47	101.65	44.12	0.000
EH-TBB	44.35	29.30	39.95	41.42	104.59	74.73	0.000
BTBPE	58.85	50.50	44.65	86.58	70.82	45.40	0.000
BEH-TEBP	56.73	36.55	80.85	60.84	78.18	39.47	0.000
DBDPE	56.08	43.10	55.58	69.11	51.41	64.50	0.311
α-HBCDD	39.15	64.00	66.85	89.37	60.82	43.13	0.000
β-HBCDD	41.70	63.50	68.65	86.63	59.94	42.63	0.000
γ-HBCDD	32.80	46.10	76.65	58.42	61.00	66.30	0.001
Σtri-hepta BDEs	43.30	18.70	40.25	51.79	100.82	74.33	0.000
ΣPBDEs	51.00	51.40	42.20	56.21	88.76	61.03	0.001
ΣHBCDDs	33.65	52.70	71.40	79.11	59.24	54.93	0.001
ΣNBFRs	51.75	35.10	64.50	59.42	75.53	56.57	0.056
ΣBFRs	47.30	48.20	58.55	54.68	85.94	56.23	0.011

We next conducted a Kruskal-Wallis test to compare mean concentrations between countries for several combined groups, viz: Σtri-hepta BDEs, ΣPBDEs, ΣHBCDDs and ΣNBFRs (Table 5.2). Not surprisingly, concentrations were highest in the US samples for both ΣPBDEs and Σtri-hepta BDEs, being significantly higher than in the other 5 countries (Figure 5.2, Figure 5.20, 5.21). Significant international differences were also observed for ΣHBCDDs, with Jordan and Spain ranked the first and second highest, respectively (Figure 5.2, Figure 5.23). However, in contrast to the observations above for individual NBFRs, concentrations of ΣNBFRs displayed no significant international

differences (p=0.056), as indicated in Figure 5.2 and more clearly in Figure 5.22. All the differences and ranks discussed above are illustrated in Figure 5.3-5.30.

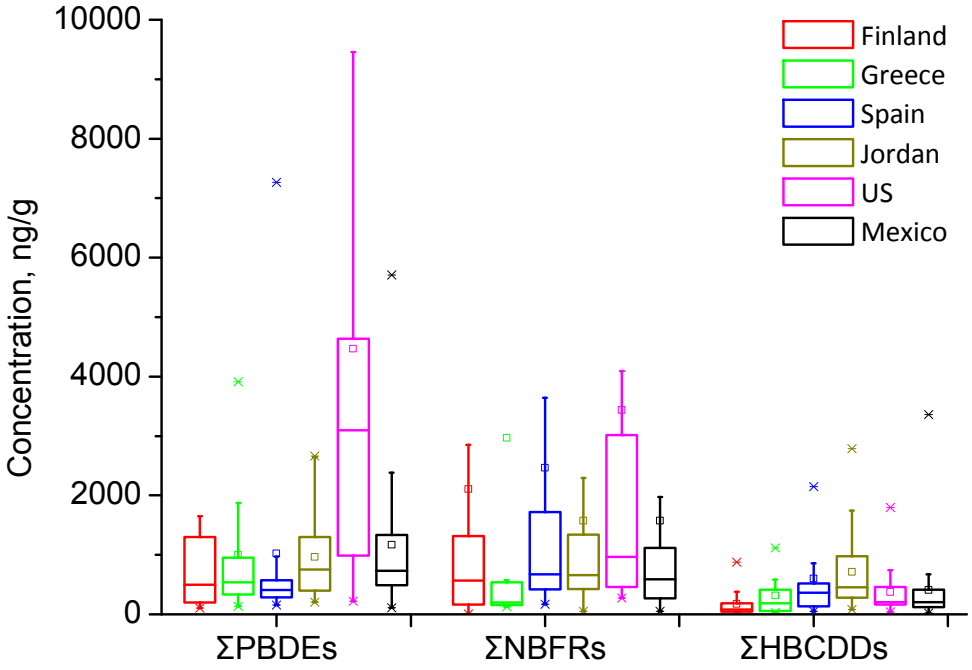


Figure 5.2: Range of concentrations (ng/g) of BFRs in house dust from different countries in this study

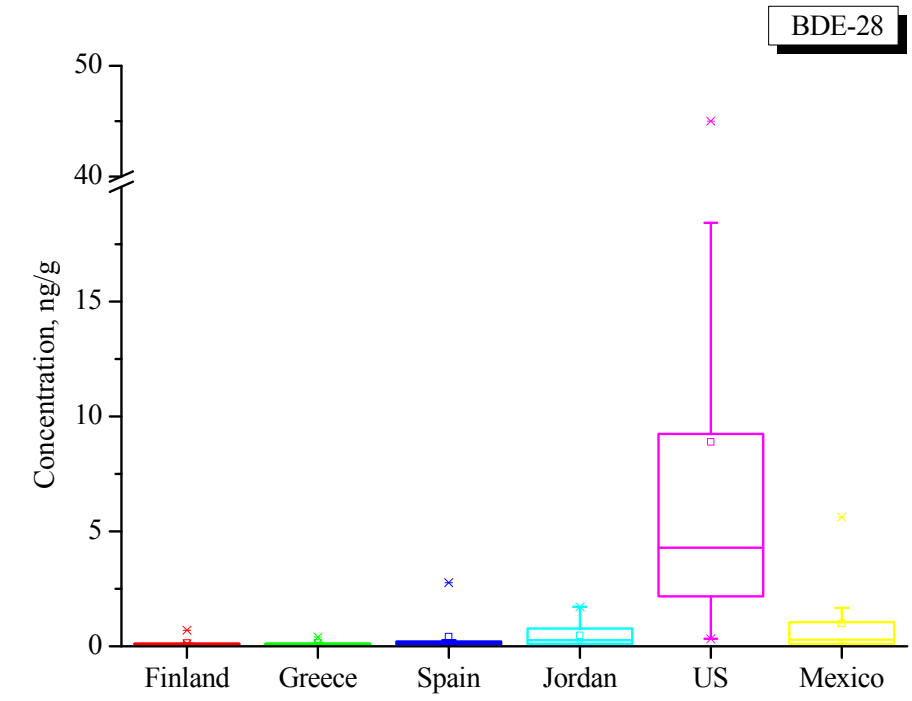


Figure 5.3: Concentrations of BDE-28 in each country

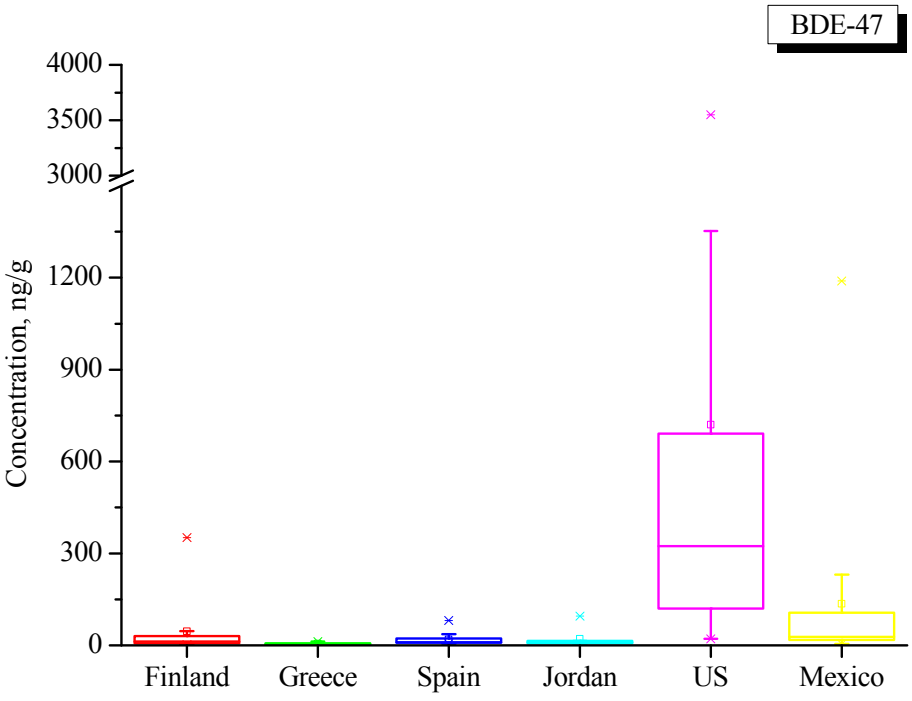


Figure 5.4: Concentrations of BDE-47 in each country

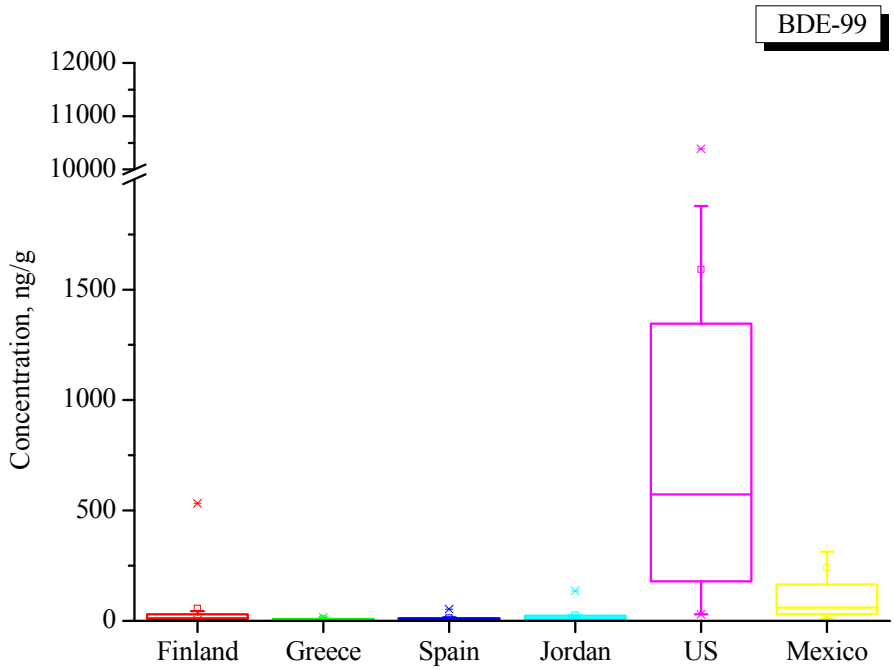


Figure 5.5: Concentrations of BDE-99 in each country

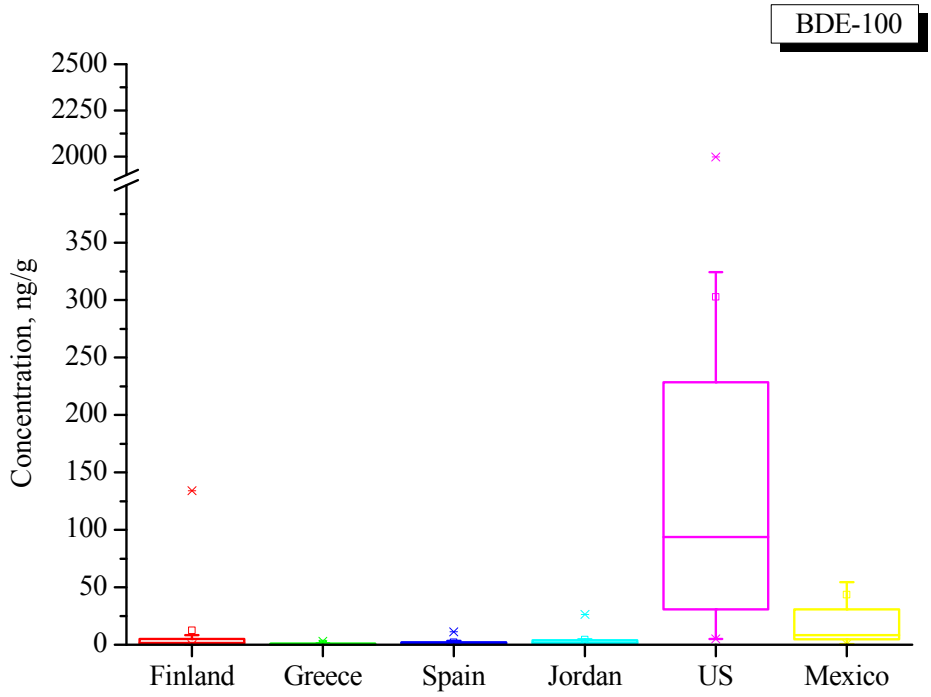


Figure 5.6: Concentrations of BDE-100 in each country

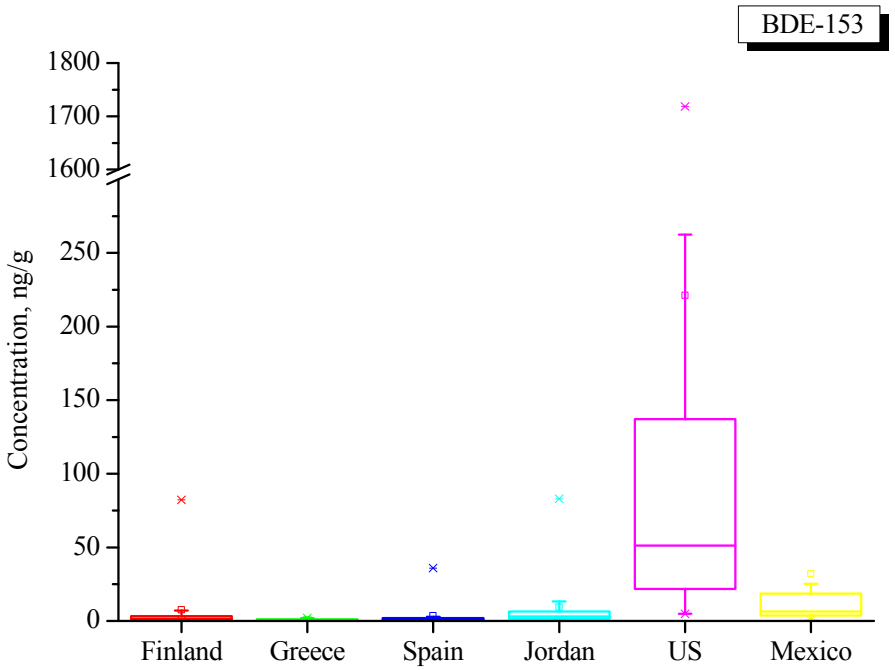


Figure 5.7: Concentrations of BDE-153 in each country

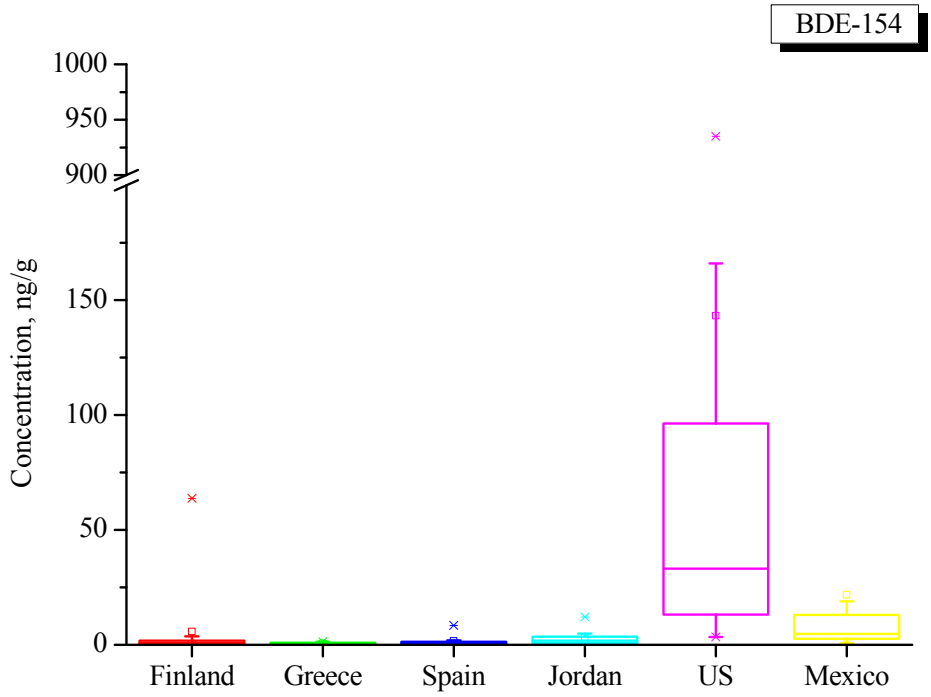


Figure 5.8: Concentrations of BDE-154 in each country

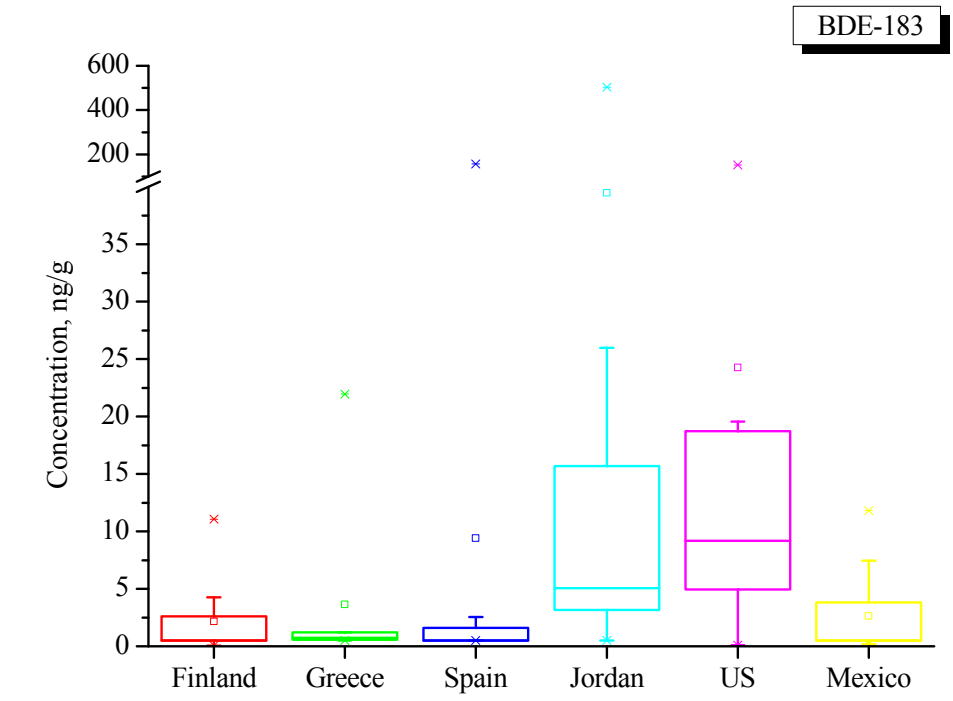


Figure 5.9: Concentrations of BDE-183 in each country

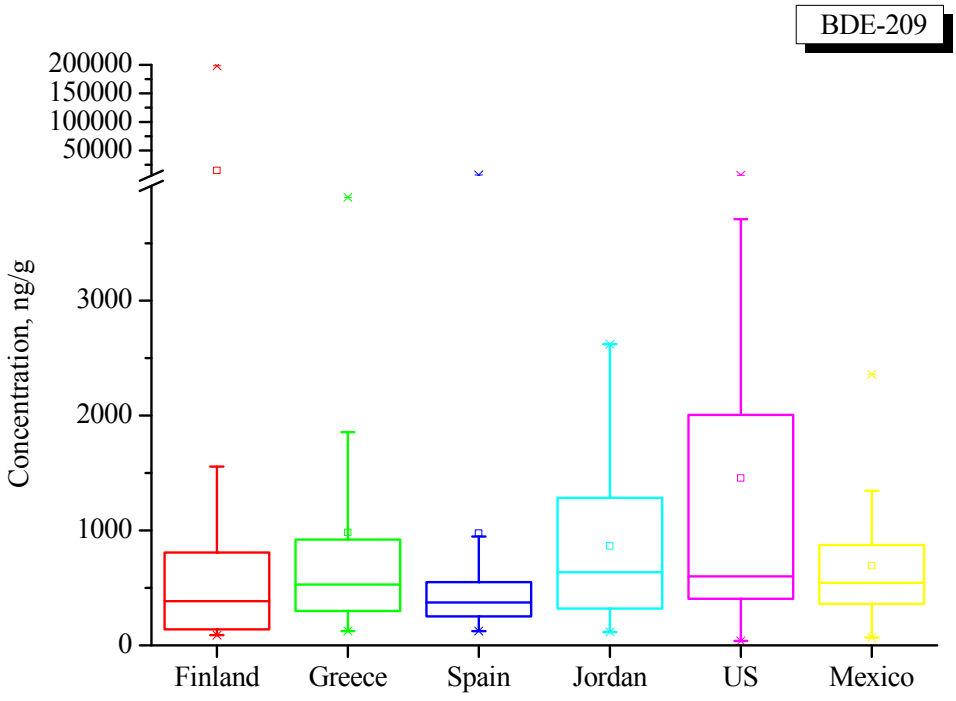


Figure 5.10: Concentrations of BDE-209 in each country

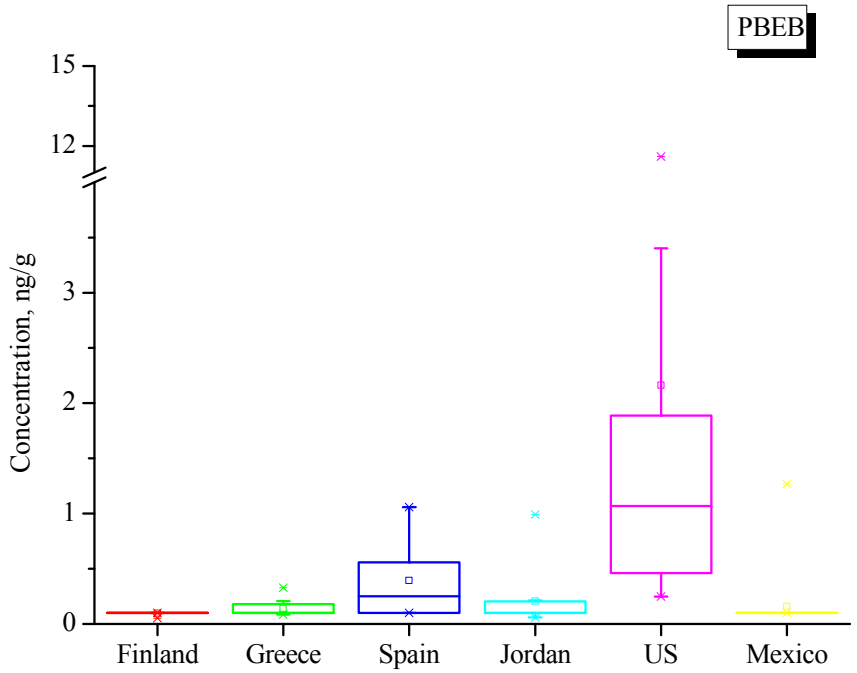


Figure 5.11: Concentrations of PBEB in each country

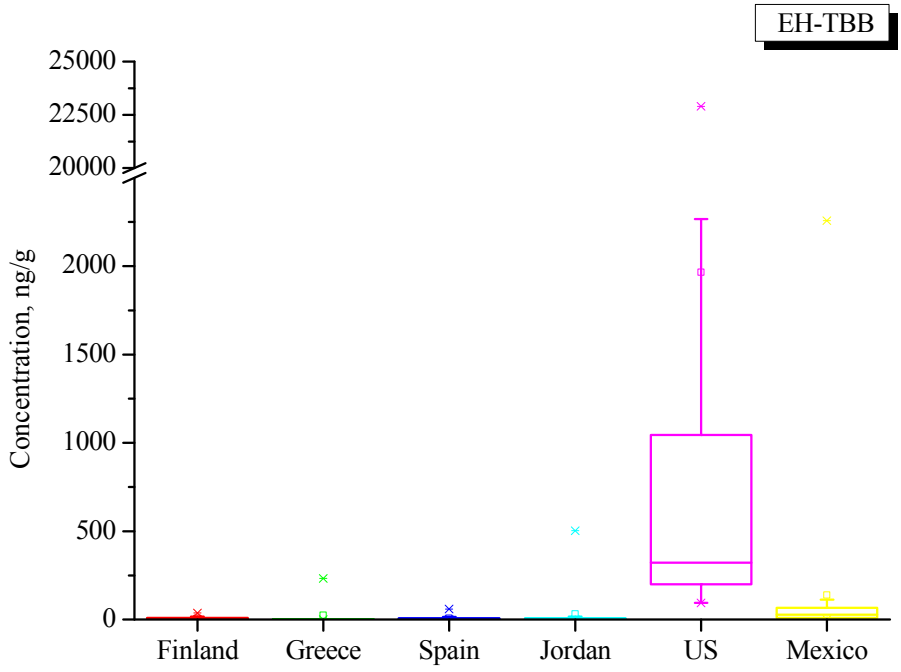


Figure 5.12: Concentrations of EH-TBB in each country

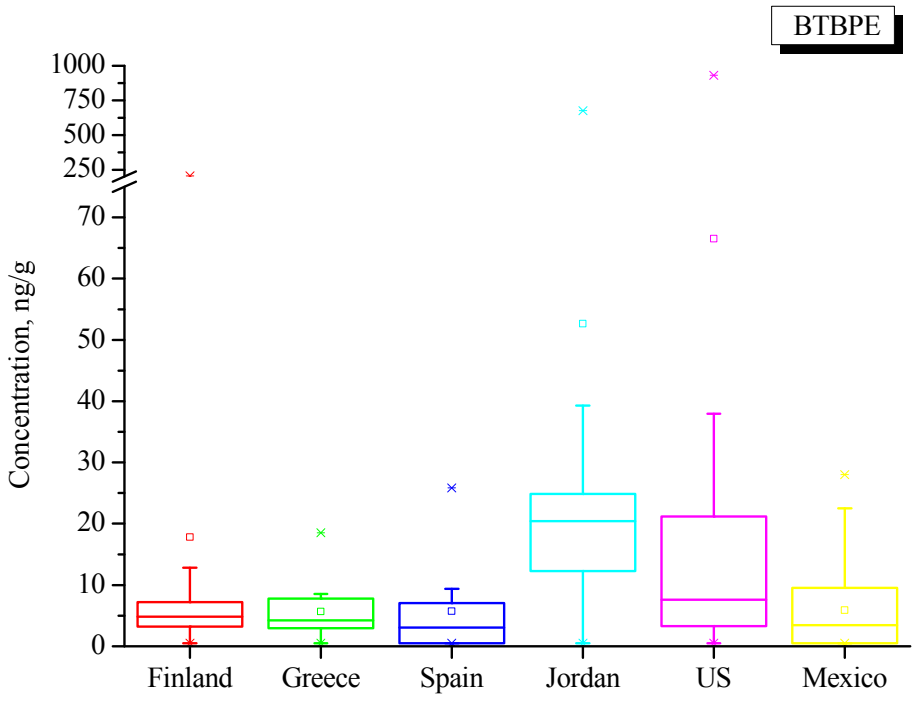


Figure 5.13: Concentrations of BTBPE in each country

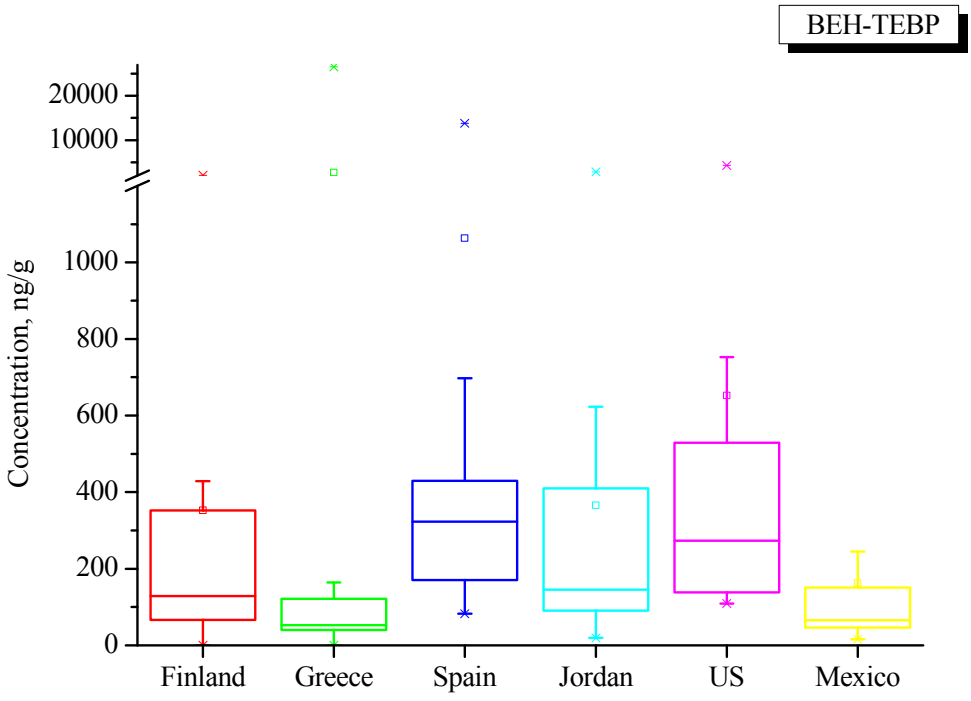


Figure 5.14: Concentrations of BEH-TEBP in each country

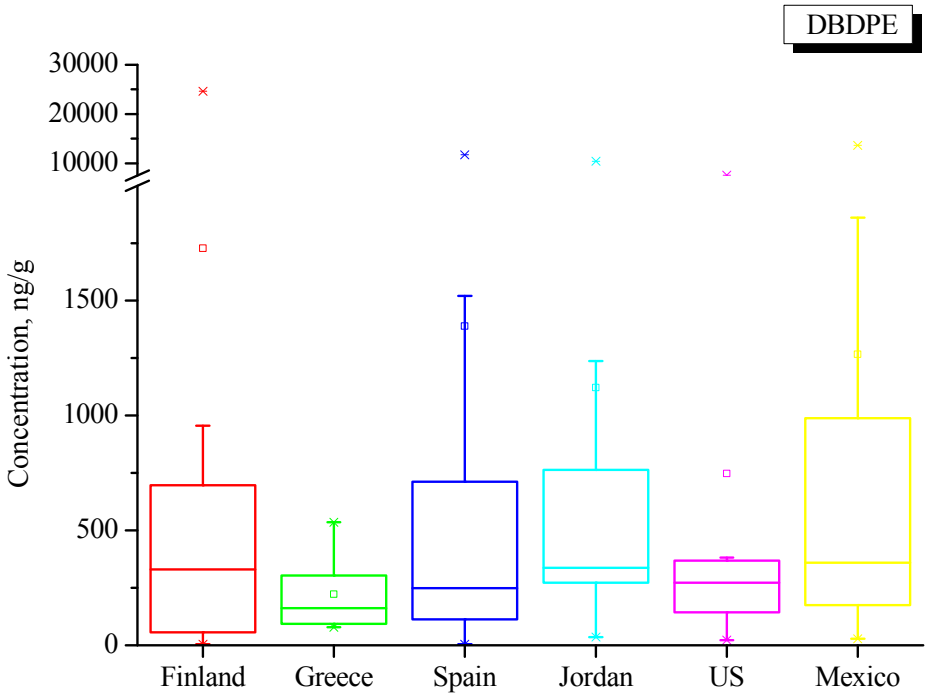


Figure 5.15: Concentrations of DBDPE in each country

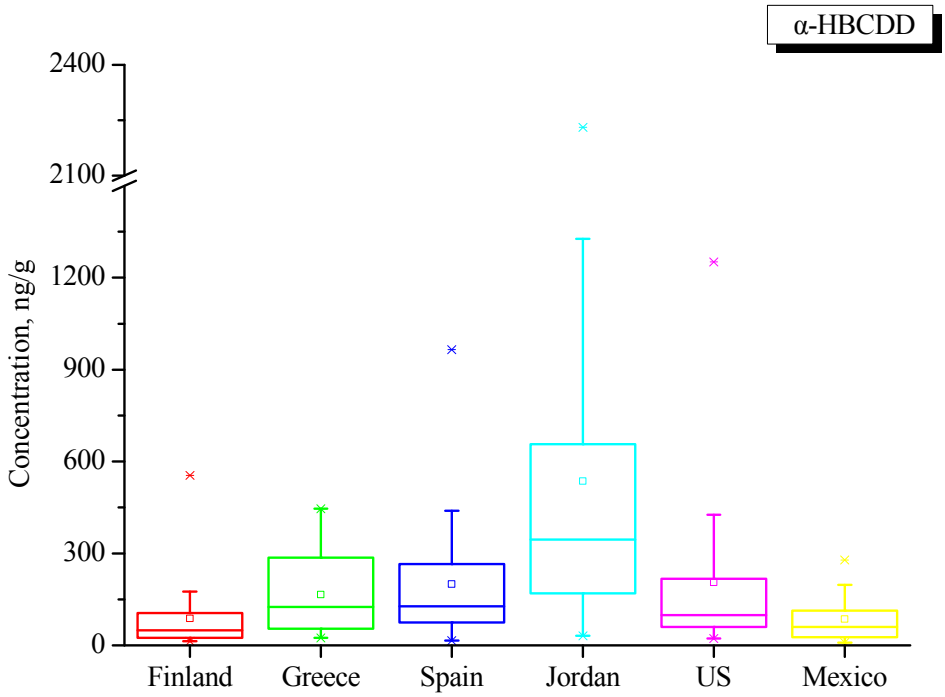


Figure 5.16: Concentrations of α-HBCDD in each country

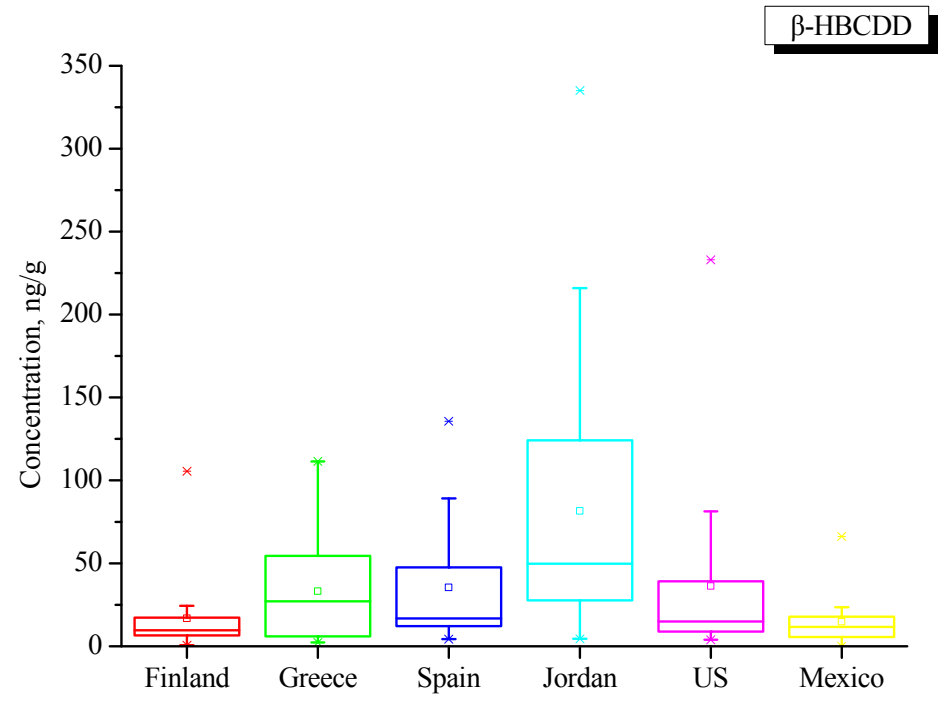


Figure 5.17: Concentrations of β-HBCDD in each country

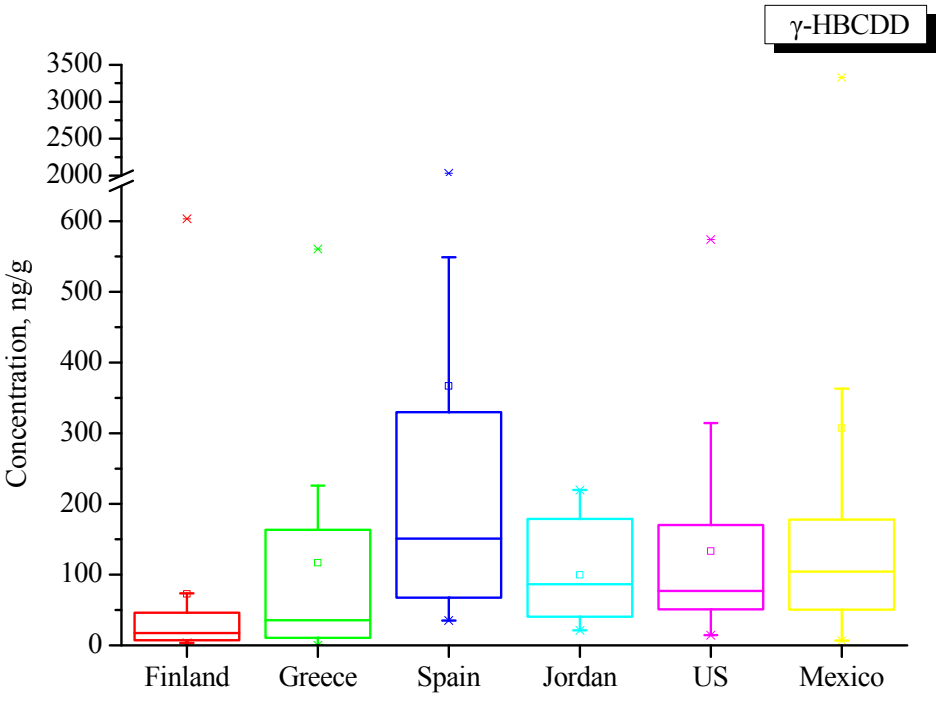


Figure 5.18: Concentrations of γ-HBCDD in each country

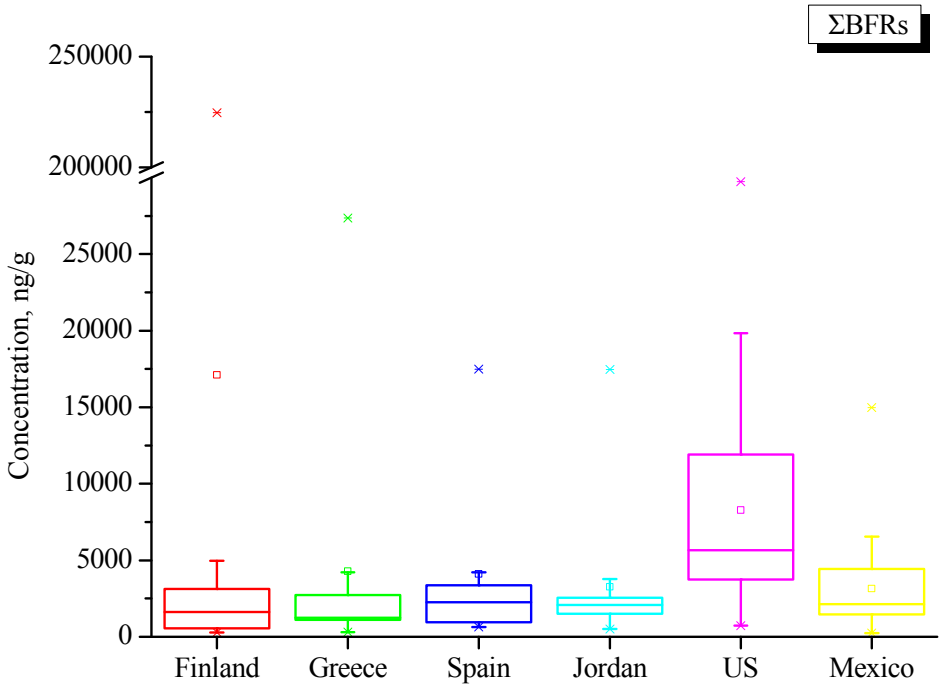


Figure 5.19: Concentrations of ΣBFRs in each country

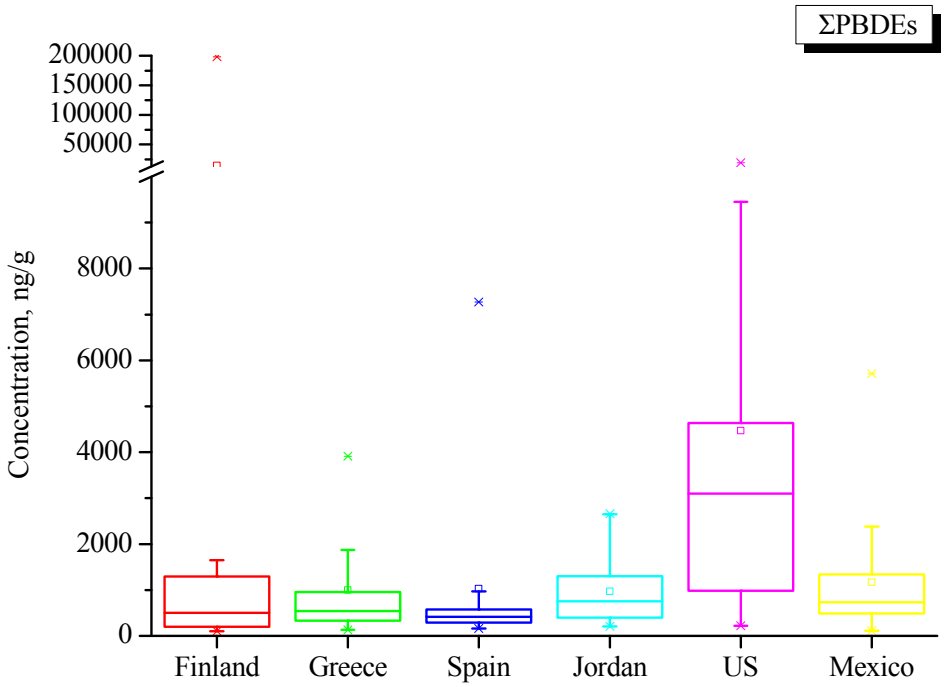


Figure 5.20: Concentrations of ΣPBDEs in each country

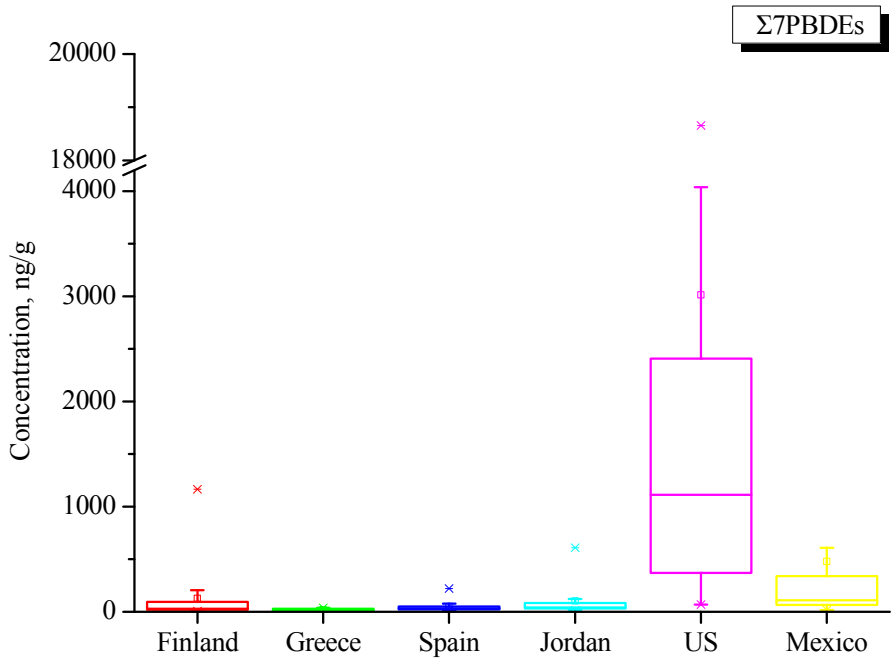


Figure 5.21: Concentrations of Σtri-hepta BDEs in each country

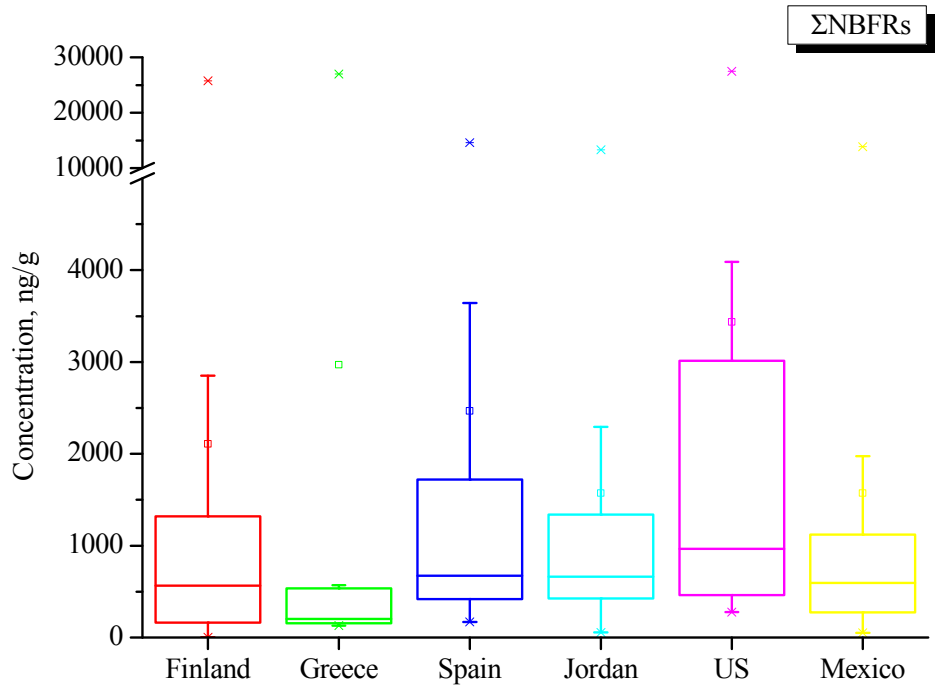


Figure 5.22: Concentrations of ΣNBFRs in each country

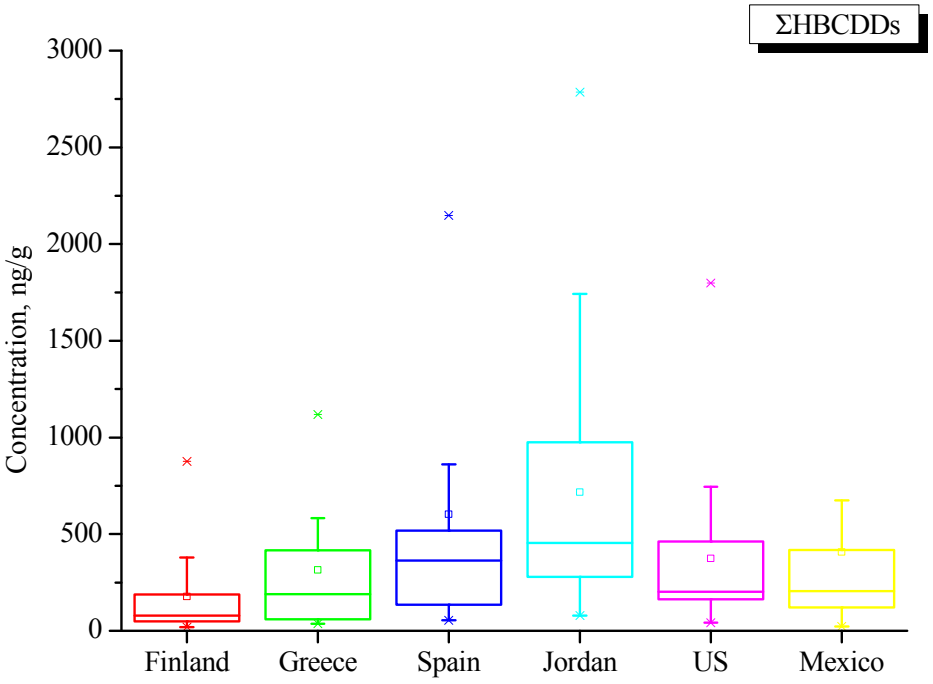


Figure 5.23: Concentrations of ΣHBCDDs in each country

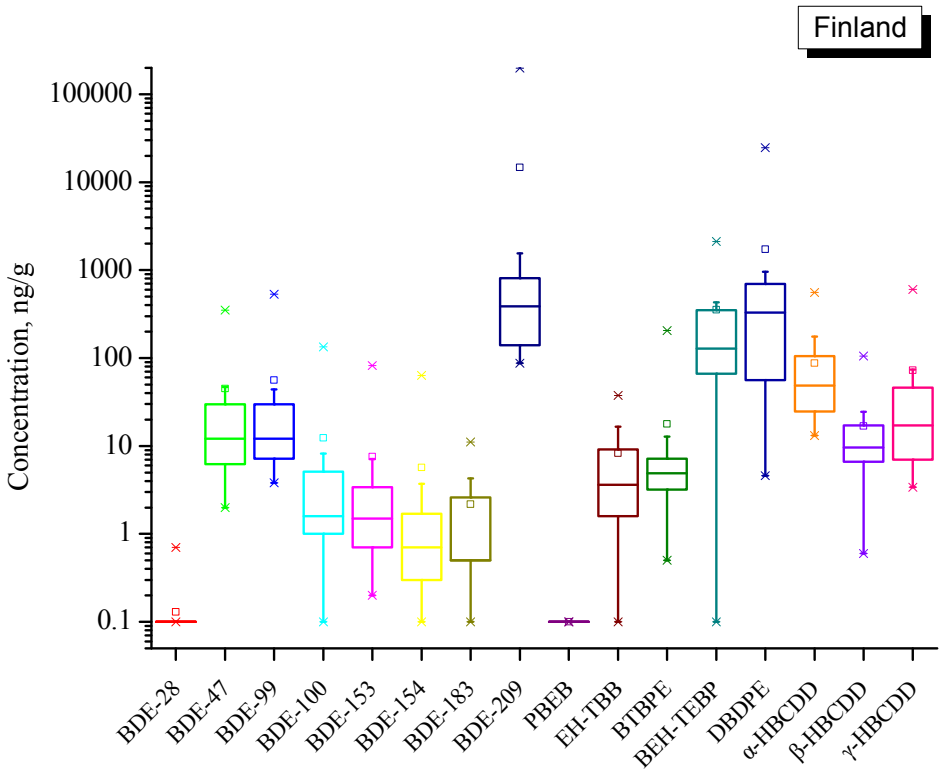


Figure 5.24: Concentration of each BFR in Finland

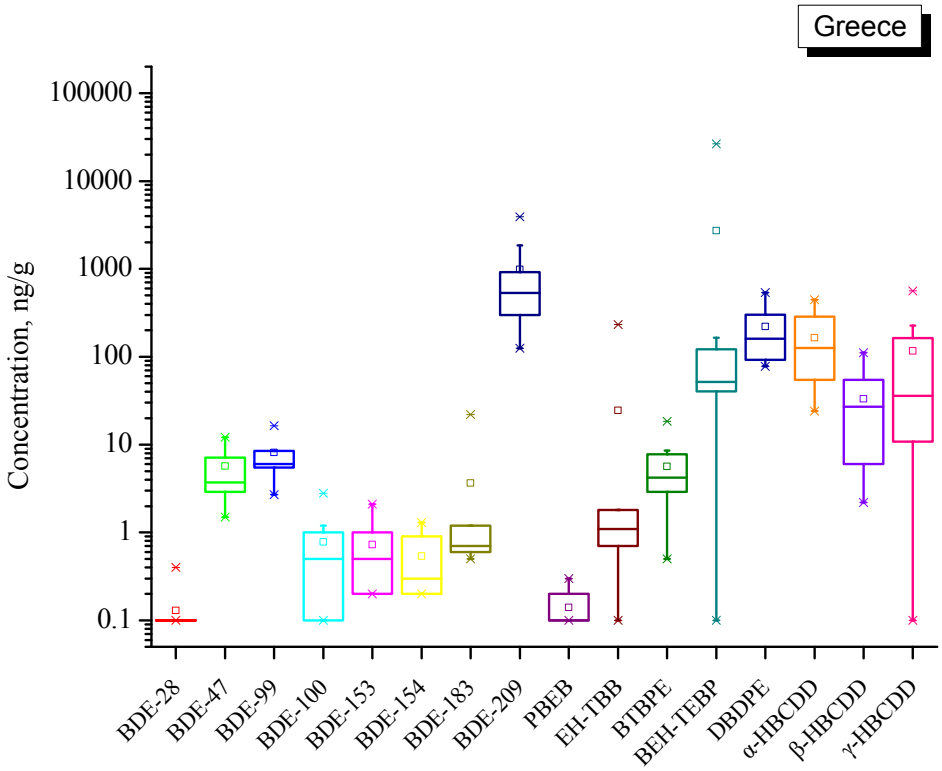


Figure 5.25: Concentration of each BFR in Greece

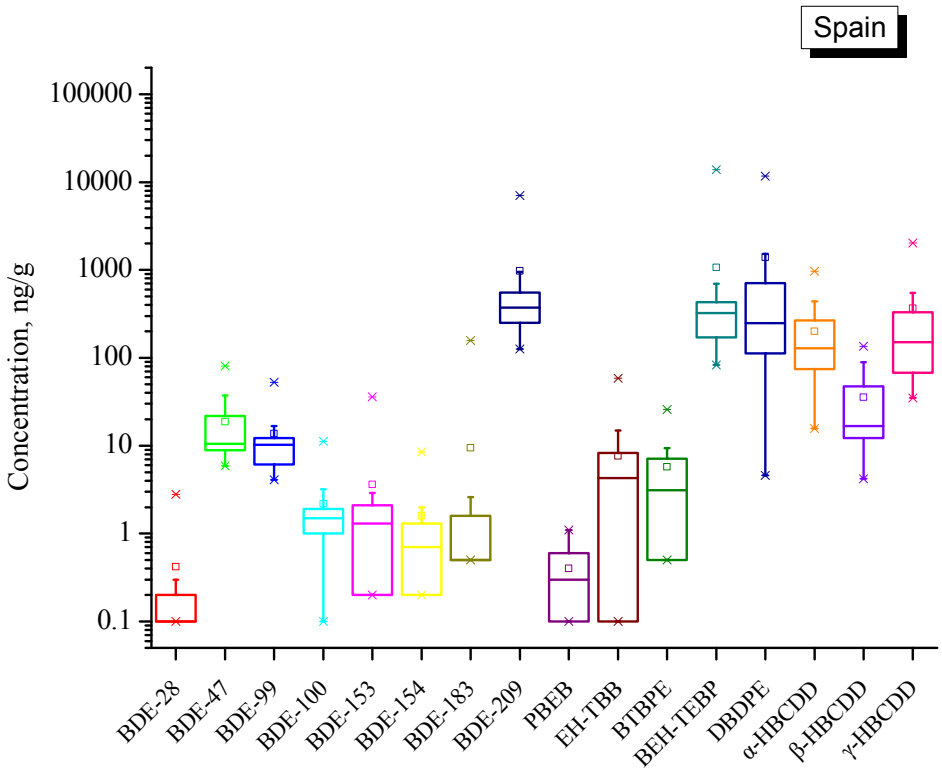


Figure 5.26: Concentration of each BFR in Spain

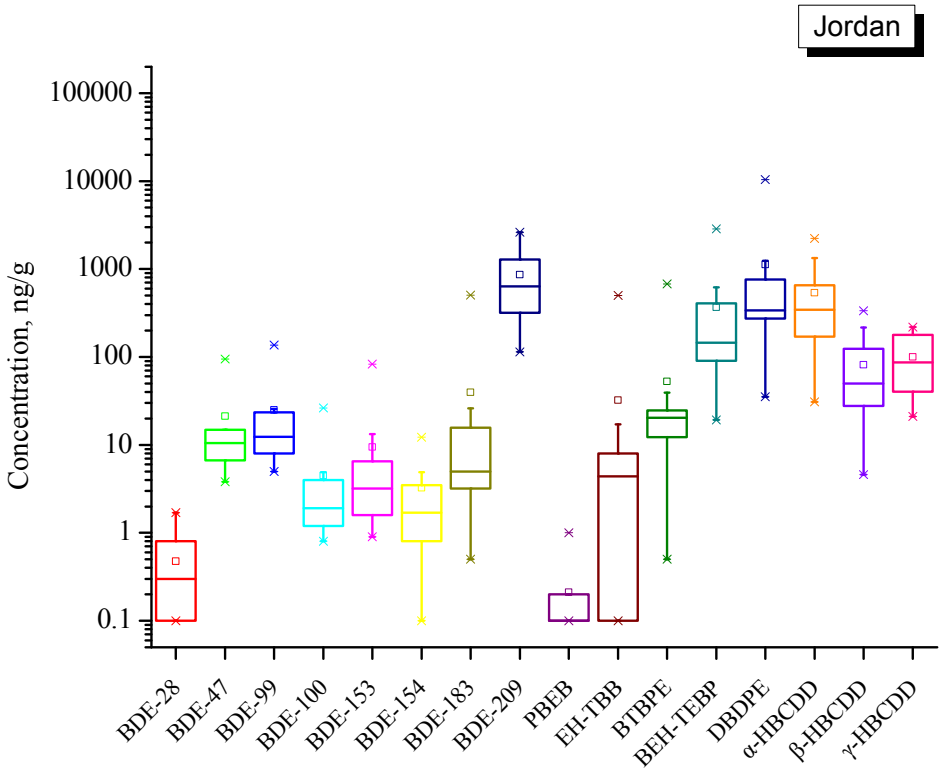


Figure 5.27: Concentration of each BFR in Jordan

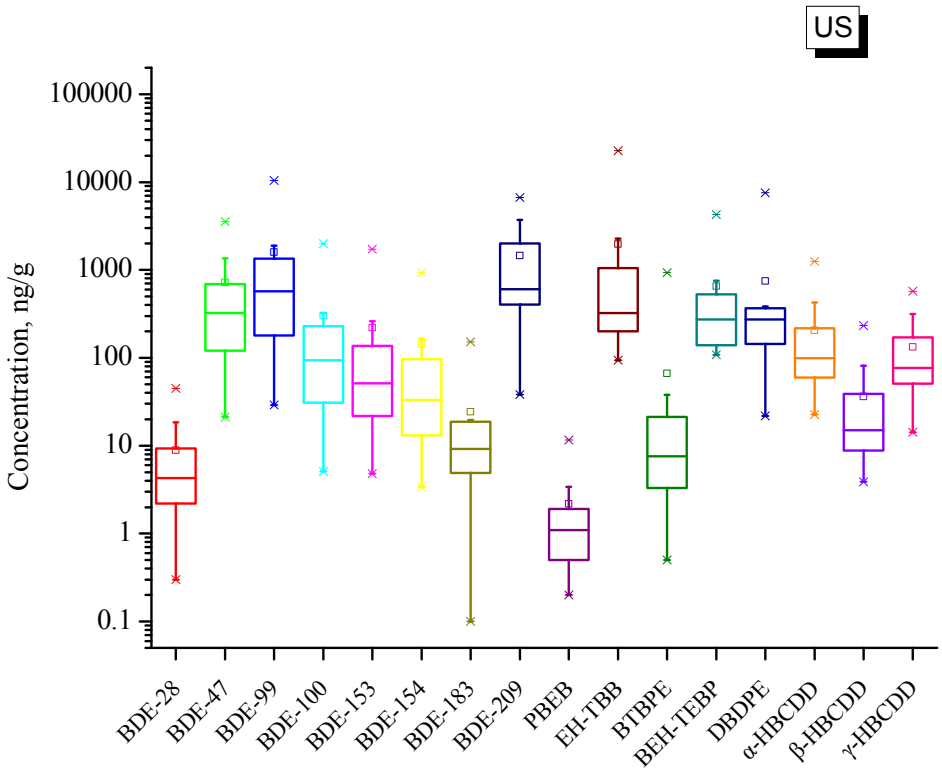


Figure 5.28: Concentration of each BFR in US

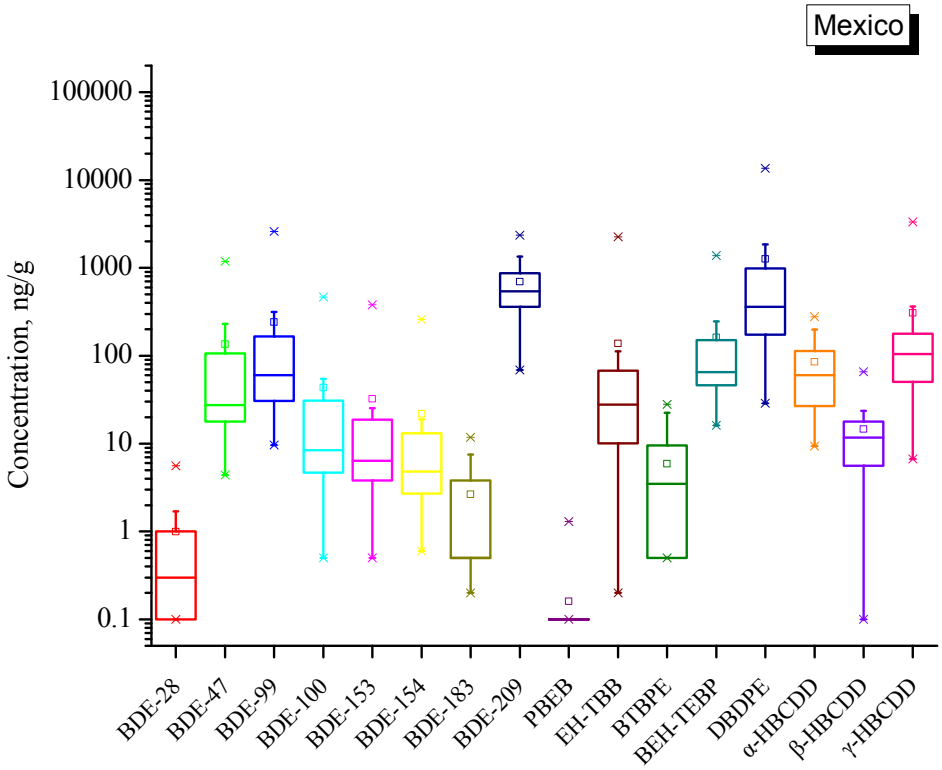


Figure 5.29: Concentration of each BFR in Mexico

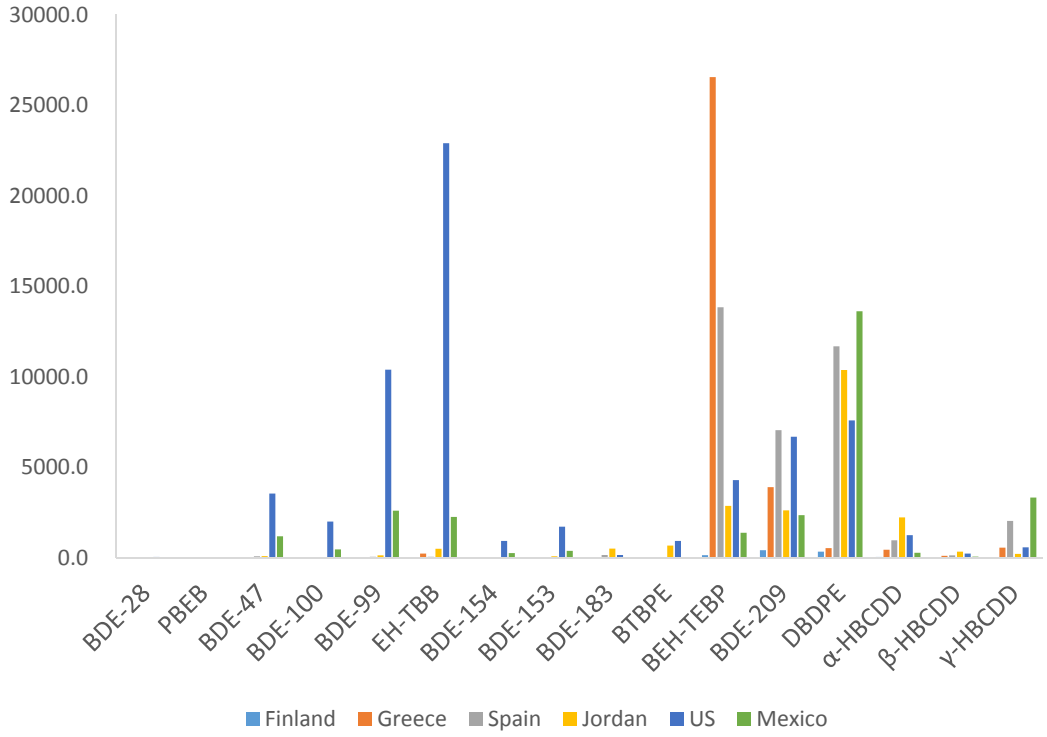


Figure 5.30: Median concentrations of target BFRs in house dust samples in each country, ng/g

For ΣBFRs, the order of mean concentrations indicated by the Kruskal-Wallis rank test were: US (85.94) > Spain (58.55) > Mexico (56.23) > Jordan (54.68) > Greece (48.20) > Finland (47.30) (Table 5.2). However, this comparison may be skewed by highly abundant compounds such as BDE-209 and BEH-TEBP. To give an equal weight to each compound for our comparison, we summed the mean ranks in each country from BDE-28 to γ-HBCDD and then divided by 16. The average of mean ranks showed a different order - i.e.: US (84.31) > Jordan (61.97) > Mexico (60.72) > Spain (52.47) > Finland (45.37) > Greece (39.71). Apart from the comparisons based on rank test, we also compared the sum of each BFR's median concentration, which showed the following result: US (2757.4 ng/g) > Jordan (1659.1 ng/g) > Spain (1322.1 ng/g) > Mexico (1306.1 ng/g) > Greece (1065.0 ng/g) > Finland (1019.4 ng/g). It can be found from these 3 comparisons that although the results of each were not identical, the trend was broadly consistent, with the US samples displaying much higher concentrations than the other countries, followed by Jordan, Spain and Mexico as second group, and then Finland and Greece the lowest.

5.3.2 Principal component analysis

To investigate international differences in the relative abundance of our target BFRs, we ran a principal component analysis (PCA). The PCA performance for all 16 compounds was disappointing, requiring 6 components to explain 80 % of the variance in our dataset (Table 5.3), which may be attributed to the poor relationship among

NBFRs and HBCDDs (Table 5.4). For the same reason, PCA of 5 NBFRs and 3 HBCDDs also yielded unsatisfactory results, needing 5 components to explain 80% variance (Table 5.5). However, focusing the PCA on the 8 PBDEs only reduced the number of variables effectively, as a result, component 1 alone explained 67 % variance, component 2 and 3 weighed very close, both explained 12.5 % variance, enabling us explain > 90 % variance using only 3 components (Table 5.6). As shown by component matrix (Table 5.7) and component plot (Figure 5.31 and 5.32), component 1 was positively related with tri-hexa BDEs which are main congeners of commercial Penta-BDE formula, and was little influenced by BDE-183 and BDE-209. In contrast, both component 2 and 3 had little to do with tri-hexa BDEs, but strongly related with BDE-183 and BDE-209 to a similar extent. The difference between component 2 and 3 was reflected by their relationship with BDE-183: component 2 was positively correlated with BDE-183 whilst component 3 negatively. Roughly, component 1 could represent commercial Penta-BDE (Figure 5.31), and component 2 represents (Deca-BDE + Octa-BDE) whilst component 3 represents (Deca-BDE – Octa-BDE) considering BDE-183 and BDE-209 was the representative congener for Octa- and Deca-BDE, respectively (Figure 5.32).

Table 5.3: Eigenvalues and variance explained of each components in principal component analysis of total BFRs

Component	Eigenvalue	% of Variance	Cumulative %
1	5.453	34.083	34.083
2	2.331	14.569	48.652
3	1.613	10.080	58.732
4	1.305	8.159	66.891
5	1.163	7.269	74.160
6	1.018	6.363	80.523
7	0.980	6.125	86.648
8	0.827	5.171	91.819
9	0.642	4.012	95.831
10	0.316	1.976	97.808
11	0.276	1.724	99.531
12	0.039	0.245	99.776
13	0.022	0.141	99.916
14	0.008	0.051	99.967
15	0.005	0.029	99.996
16	0.001	0.004	100.000

Table 5.4: Correlation Matrix of BFRs

	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209
BDE-28	1.000	0.746	0.632	0.624	0.604	0.617	0.021	-0.034
BDE-47	0.746	1.000	0.959	0.966	0.944	0.972	0.038	-0.031
BDE-99	0.632	0.959	1.000	0.997	0.990	0.989	0.052	-0.028
BDE-100	0.624	0.966	0.997	1.000	0.990	0.996	0.050	-0.028
BDE-153	0.604	0.944	0.990	0.990	1.000	0.984	0.104	-0.026
BDE-154	0.617	0.972	0.989	0.996	0.984	1.000	0.059	-0.029
BDE-183	0.021	0.038	0.052	0.050	0.104	0.059	1.000	0.002
BDE-209	-0.034	-0.031	-0.028	-0.028	-0.026	-0.029	0.002	1.000
PBEB	0.509	0.221	0.138	0.122	0.102	0.112	-0.008	-0.024
EH-TBB	0.098	0.090	0.075	0.061	0.040	0.047	-0.003	-0.020
BTBPE	0.006	-0.009	-0.003	-0.011	0.009	-0.009	0.300	0.098
BEH-TEBP	0.009	-0.027	-0.025	-0.027	-0.026	-0.027	0.011	0.000
DBDPE	0.010	-0.034	-0.051	-0.047	-0.050	-0.050	0.009	0.660
α-HBCDD	0.050	-0.004	-0.036	-0.027	-0.036	-0.030	0.094	-0.021
β-HBCDD	0.065	0.015	-0.024	-0.014	-0.027	-0.018	0.076	0.003
γ-HBCDD	-0.045	-0.043	-0.044	-0.044	-0.040	-0.042	-0.029	-0.024

Table 5.4 (continued): Correlation Matrix of BFRs

	PBEB	EH-TBB	BTBPE	BEH-TEBP	DBDPE	α-HBCDD	β-HBCDD	γ-HBCDD
BDE-28	0.509	0.098	0.006	0.009	0.010	0.050	0.065	-0.045
BDE-47	0.221	0.090	-0.009	-0.027	-0.034	-0.004	0.015	-0.043
BDE-99	0.138	0.075	-0.003	-0.025	-0.051	-0.036	-0.024	-0.044
BDE-100	0.122	0.061	-0.011	-0.027	-0.047	-0.027	-0.014	-0.044
BDE-153	0.102	0.040	0.009	-0.026	-0.050	-0.036	-0.027	-0.040
BDE-154	0.112	0.047	-0.009	-0.027	-0.050	-0.030	-0.018	-0.042
BDE-183	-0.008	-0.003	0.300	0.011	0.009	0.094	0.076	-0.029
BDE-209	-0.024	-0.020	0.098	0.000	0.660	-0.021	0.003	-0.024
PBEB	1.000	0.148	-0.003	0.017	-0.013	0.023	0.014	-0.044
EH-TBB	0.148	1.000	0.011	0.129	-0.030	-0.033	-0.032	0.015
BTBPE	-0.003	0.011	1.000	0.010	0.009	0.391	0.377	-0.018
BEH-TEBP	0.017	0.129	0.010	1.000	0.009	-0.024	-0.037	-0.052
DBDPE	-0.013	-0.030	0.009	0.009	1.000	0.161	0.193	-0.015
α-HBCDD	0.023	-0.033	0.391	-0.024	0.161	1.000	0.976	0.049
β-HBCDD	0.014	-0.032	0.377	-0.037	0.193	0.976	1.000	0.052
γ-HBCDD	-0.044	0.015	-0.018	-0.052	-0.015	0.049	0.052	1.000

Table 5.5: Eigenvalues and variance explained of each components in principal component analysis of NBFRs and HBCDDs

Component	Eigenvalue	% of Variance	Cumulative %
1	2.266	28.328	28.328
2	1.214	15.181	43.509
3	1.030	12.879	56.389
4	0.984	12.300	68.689
5	0.978	12.225	80.914
6	0.799	9.985	90.899
7	0.705	8.808	99.707
8	0.023	0.293	100.000

Table 5.6: Eigenvalues and variance explained of each components in principal component analysis of PBDEs

Component	Eigenvalue	% of Variance	Cumulative %
1	5.393	67.416	67.416
2	1.005	12.557	79.972
3	0.995	12.434	92.406
4	0.554	6.921	99.327
5	0.039	0.490	99.817
6	0.009	0.108	99.925
7	0.005	0.065	99.990
8	0.001	0.010	100.000

Table 5.7: Component matrix (first 3 components) of principal component analysis of PBDEs

	Component 1	Component 2	Component 3
BDE-28	0.724	-0.061	0.028
BDE-47	0.986	-0.023	0.028
BDE-99	0.988	-0.001	0.017
BDE-100	0.990	-0.003	0.018
BDE-153	0.980	0.040	-0.018
BDE-154	0.987	0.004	0.011
BDE-183	0.071	0.735	-0.672
BDE-209	-0.037	0.677	0.735

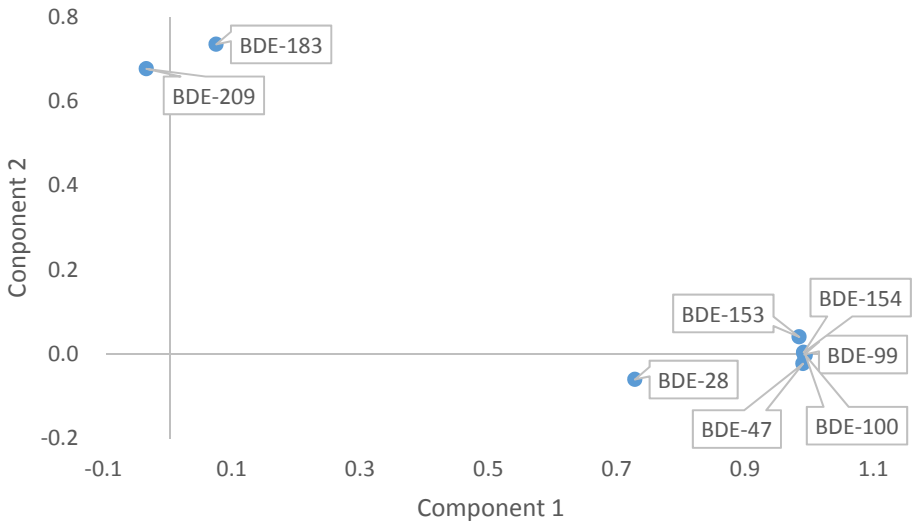


Figure 5.31: Principal Component Plot of Component 1 versus Component 2 for PBDEs in this study

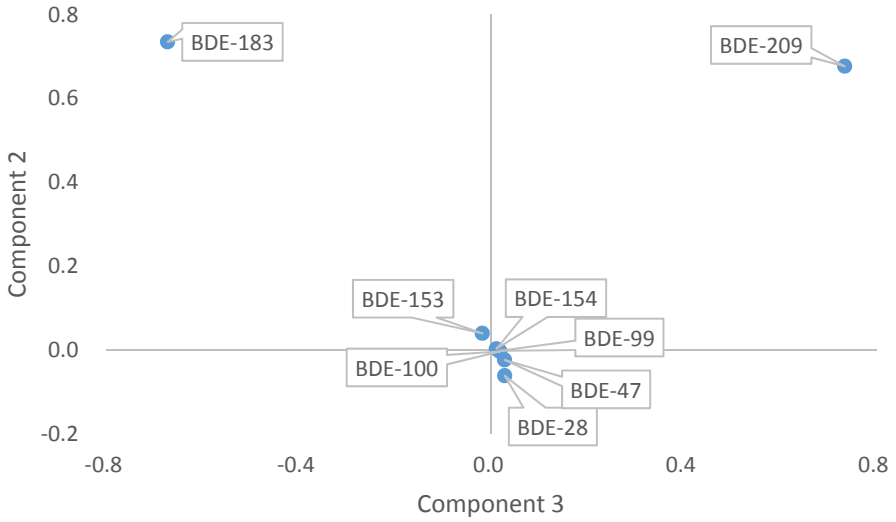


Figure 5.32: Principal Component Plot of Component 3 versus Component 2 for PBDEs in this study

Further, we calculated scores of components 1, 2 and 3 for all 116 samples and drew scatter plots by country (Figure 5.33~5.36). Interestingly, in the component 1 vs component 2 plot (Figure 5.33), all data points distribute along the axis; and similarly, in Figure 5.35, all data points distribute along the ±45° line. As demonstrated above, component 1 represent Penta-BDE and component 2 represents the sum of Octa- and Deca-BDE. The along-axis-distributed data points indicate that, for a given house, Penta-BDE and (Octa-BDE + Deca-BDE) are not both elevated i.e. when concentrations of Penta-BDE was high in one house, concentrations of Octa- and Deca-BDE will be low, and vice versa. A plot drawn based on components 2 and 3 further distinguished Octa- and Deca-BDE (Figure 5.35). It is easy to demonstrate mathematically that, when component 3 (X axis, y=0) represents (Deca-BDE – Octa-BDE) and component 2 (Y axis, x=0) represents (Deca-BDE + Octa-BDE), the +45º

line (x-y=0) represents Deca-BDE and the -45º line (x+y=0) represents Octa-BDE. So similarly to Figure 5.33, the data points distributing along the ±45° line in Figure 5.35 indicate Octa-BDE and Deca-BDE are not both dominant in the same house also. Interpreting Figure 5.33 and 5.35 together, we can demonstrate that dust samples from a given house are only dominated by one PBDE formula, which implies in one house, there is a major source treated by one PBDE formula, or that all sources in that house are treated with the same PBDE formula.

With respect to the international dust comparison, the data from US and Mexico lie along the X axis in Figure 5.33, which is consistent with the conclusion of Kruskal-Wallis test that US and Mexican samples displayed the 1st and 2nd highest concentrations of Penta-BDE respectively. The points lying along the Y axis of Figure 5.33 are mainly Jordanian samples, as well as several samples from Finland, the US and 1 Spanish sample. Figure 5.35 further separates points lying along the Y axis in Figure 5.33. All Jordanian samples lie along the Octa-BDE line, as well as several US points and 1 Spanish sample. In contrast, the 2 Finnish samples lie along the Deca-BDE line. The distribution pattern of Jordanian samples indicates a higher Octa-BDE consumption in Jordan, which is also consistent with the highest maximum and mean BDE-183 concentration in Jordan compared with other countries (Figure 5.9), and the 2nd highest median concentration (Figure 5.9) and Kruskal-Wallis test rank (Table 5.2). Interestingly, Al-Omran and Harrad (2016) investigated BFR concentrations in Iraqi

dust samples, reporting an elevated BDE-183 concentration also. Thus it is reasonable to infer that there is a greater Octa-BDE consumption in the Middle East. The 2 US samples lying along the Octa-BDE line indicate that although most US samples are dominated by Penta-BDE, some outliers dominated by Octa-BDE exist. The Finnish samples lying along the Deca-BDE line are consistent with the results displayed in Table 5.1 and Figure 5.12 where extremely high BDE-209 concentrations were observed for Finnish samples. As all PCA scores were based on normalised data, it provides a good comparison of PBDE patterns between dust from different countries. Although from the point of absolute concentration, BDE-209 was the highest in every country investigated (Table 5.1, Figure 5.24~5.29), the PCA helps us better identify a relatively high concentration of Penta-BDE in US and Mexico, and Octa-BDE in Jordan.

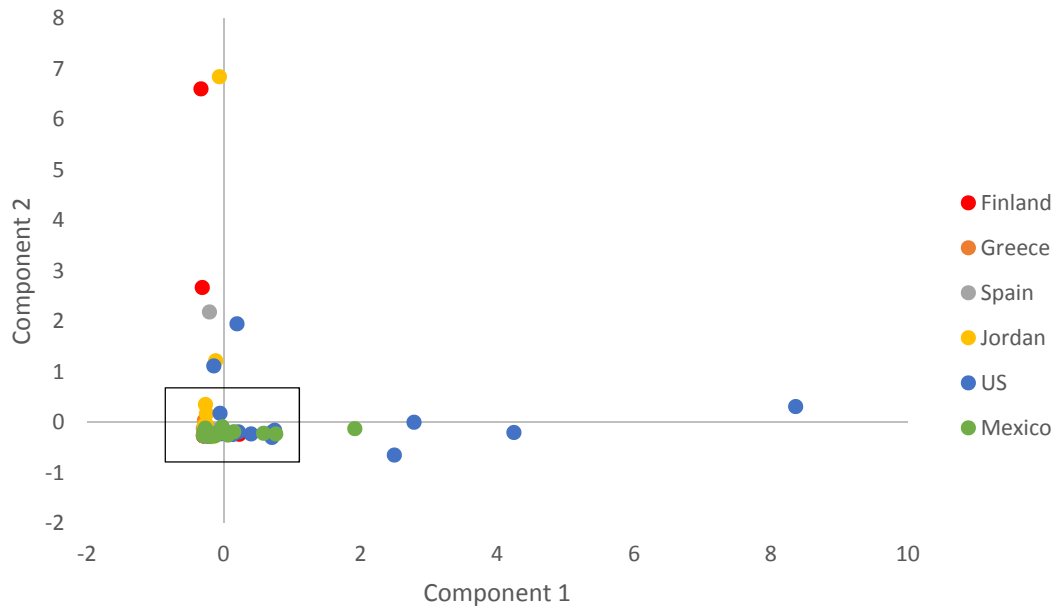


Figure 5.33: Plot of scores for components 1 and 2 for PBDEs in this study

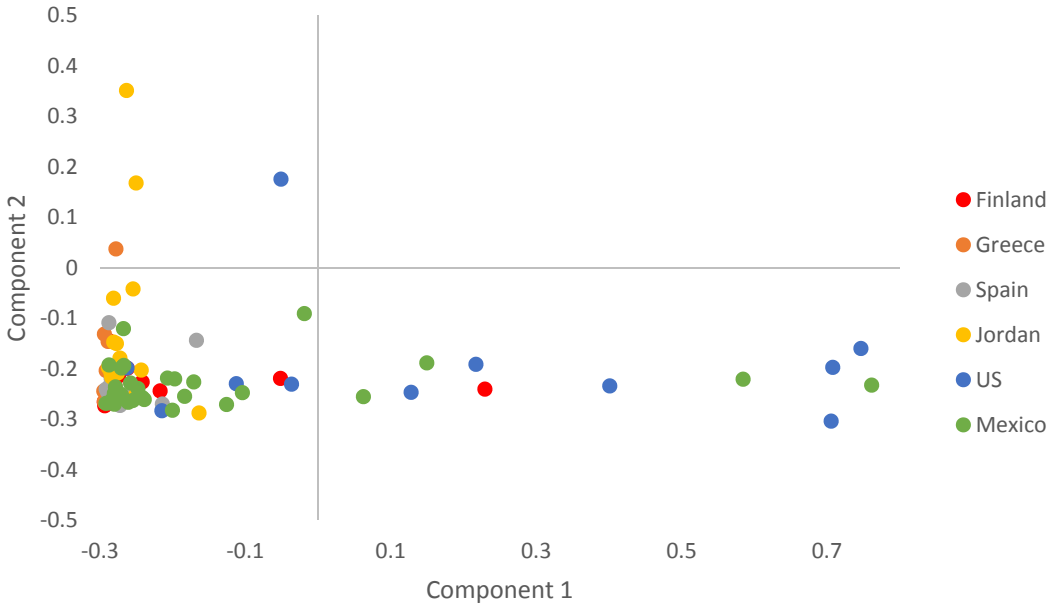


Figure 5.34: Plot of scores for components 1 and 2 for PBDEs in this study (partly magnified)

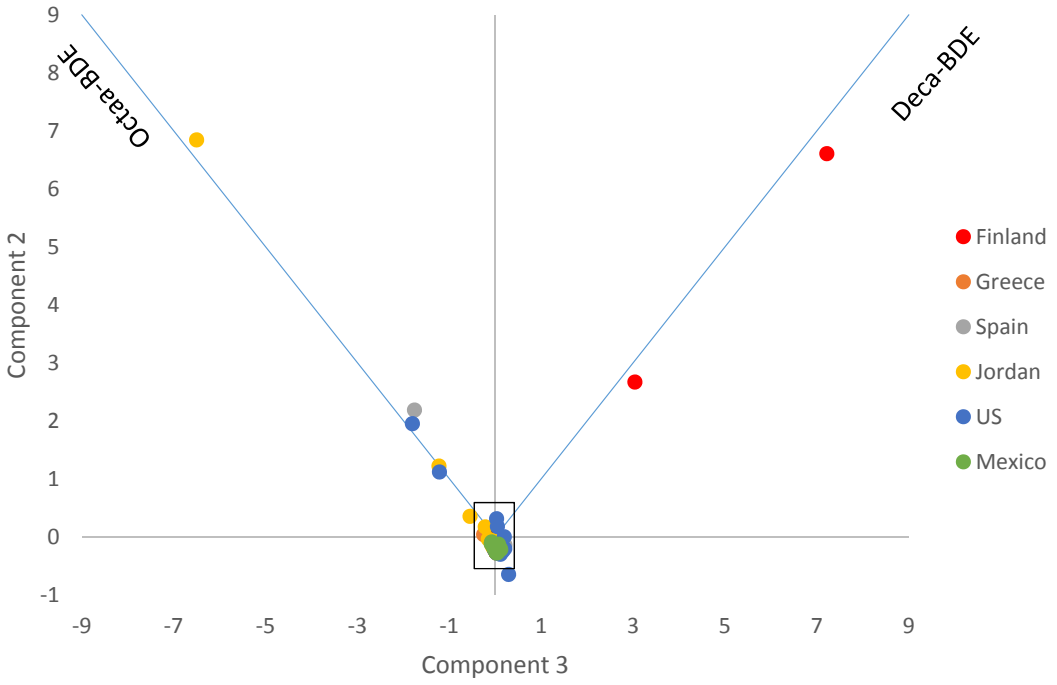


Figure 5.35: Plot of scores for components 3 and 2 for PBDEs in this study

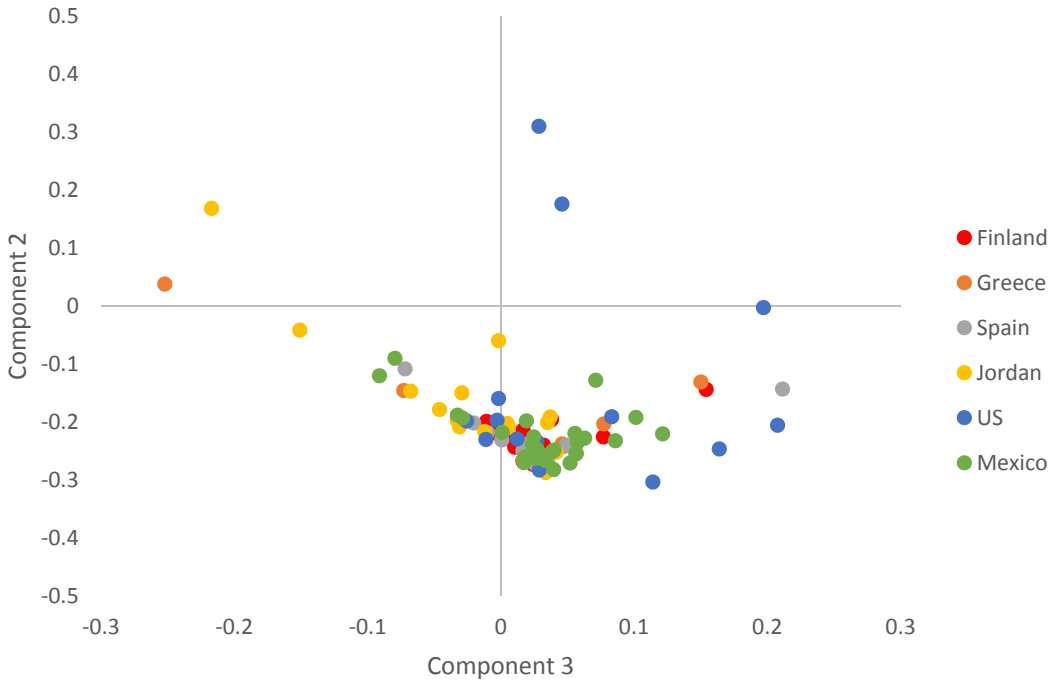


Figure 5.36: Plot of scores for components 3 and 2 for PBDEs in this study (partly magnified)

5.4 Implications for human exposure

To estimate exposure via dust ingestion, it was assumed that on average adults and toddlers ingest 20 and 50 mg dust/day respectively while under a high exposure scenario adults and toddlers ingest 50 and 200 mg dust/day respectively (Jones-Otazo et al., 2005). Exposure estimates were generated for the 4 main PBDEs under low, median and high exposure scenarios. These were respectively: 5th percentile dust concentration, average dust ingestion rate (low), median dust concentration, average dust ingestion rate (median), and 95th percentile dust concentration, high dust ingestion rate (high). Body weights of 70 kg and 10 kg for adults and toddlers respectively were assumed to calculate exposure per unit body weight (Table 5.4). Previous studies have investigated FR exposure via dust ingestion. Harrad et al. (2008) estimated daily PBDE,

DBDPE and BTBPE exposure via dust ingestion for UK adults and toddlers based on BFR concentrations in home, office and car dust. They reported BDE-209 exposure under a median exposure scenario to be 3.3 ng/kg bw/day for adult and 61 ng/kg bw/day for toddler, while under a high exposure scenario intakes were 8.3 and 240 ng/kg bw/day for adults and toddlers respectively. Compared with BDE-209, ingestion of other BFRs was negligible, lower than 1 ng/kg bw/day. Sjödin et al. (2008) estimated tetra-deca BDE exposure via dust ingestion in 4 countries: UK, US, Germany and Australia. Similar to the findings of Harrad et al. (2008), BDE-209 dominated PBDE exposure, with ranges of <0.01-85, <0.01-33, <0.01-0.64, <0.01-20 ng/kg bw/day exposure for adults in UK, US, Germany and Australia, respectively. Exposure to tetra-hepta BDEs was higher in US and Australia, ranging around <0.01-6 ng/kg bw/day for each congener, with corresponding data in UK and Germany around <0.01-0.5 ng/kg bw/day. Sun et al. (2016) measured PBDE concentrations in indoor dust and air of Zhejiang, China, and estimated relevant exposure. ΣPBDE exposures for adult in home were estimated as 0.1 ng/kg bw/day via dust ingestion. For toddlers, exposure was an estimated 2.4 ng/kg bw/day. Exposure in this study is comparable with previous studies, but far below compared with the US EPA's reference dose (120 ng/kg bw/day for BDE-47, 100 ng/kg bw/day for BDE-99, 150 ng/kg bw/day for BDE-153 and 7,000 ng/kg bw/day for BDE-209).

Table 5.4: PBDE exposure via dust ingestion (ng/kg bw/day) for adults and toddlers in different countries

			BDE-47		BDE-99		BDE-153		BDE-209	
			Adult	Toddler	Adult	Toddler	Adult	Toddler	Adult	Toddler
Finland	Mean ingestion	Low	<0.01	0.02	<0.01	0.03	<0.01	<0.01	0.03	0.44
		Median	<0.01	0.06	<0.01	0.06	<0.01	0.01	0.12	2.10
		High	0.06	0.98	0.07	1.3	0.01	0.18	26	450
	High ingestion	Low	<0.01	0.09	<0.01	0.12	<0.01	0.01	0.06	1.77
		Median	0.01	0.25	0.01	0.24	<0.01	0.03	0.30	8.39
		High	0.14	3.9	0.19	5.2	0.03	0.73	64	1800
Greece	Mean ingestion	Low	<0.01	0.01	<0.01	0.02	<0.01	<0.01	0.04	0.77
		Median	<0.01	0.02	<0.01	0.03	<0.01	<0.01	0.17	3.0
		High	<0.01	0.06	<0.01	0.08	<0.01	0.01	0.85	15
	High ingestion	Low	<0.01	0.04	<0.01	0.08	<0.01	0.01	0.11	3.1
		Median	<0.01	0.09	<0.01	0.14	<0.01	0.01	0.43	12
		High	0.01	0.24	0.01	0.33	<0.01	0.04	2.1	60
Spain	Mean ingestion	Low	<0.01	0.03	<0.01	0.02	<0.01	<0.01	0.05	0.83
		Median	<0.01	0.05	<0.01	0.05	<0.01	0.01	0.11	1.9
		High	0.01	0.22	0.01	0.20	<0.01	0.07	1.4	25
	High ingestion	Low	<0.01	0.12	<0.01	0.08	<0.01	0.01	0.12	3.3
		Median	0.01	0.21	0.01	0.21	<0.01	0.03	0.27	7.6
		High	0.03	0.88	0.03	0.80	0.01	0.28	3.5	98
Jordan	Mean ingestion	Low	<0.01	0.02	<0.01	0.03	<0.01	0.01	0.03	0.61
		Median	<0.01	0.05	<0.01	0.06	<0.01	0.02	0.18	3.2

			BDE-47		BDE-99		BDE-153		BDE-209	
			Adult	Toddler	Adult	Toddler	Adult	Toddler	Adult	Toddler
US		High	0.02	0.42	0.03	0.47	0.01	0.18	0.74	13
	High ingestion	Low	<0.01	0.08	<0.01	0.11	<0.01	0.02	0.09	2.5
		Median	0.01	0.21	0.01	0.25	<0.01	0.06	0.45	13
		High	0.06	1.67	0.07	1.87	0.03	0.72	1.9	52
	Mean ingestion	Low	0.02	0.30	0.02	0.36	<0.01	0.03	0.05	0.89
		Median	0.09	1.6	0.16	2.9	0.01	0.26	0.17	3.0
		High	0.77	14	1.6	28	0.25	4.43	1.2	22
	High ingestion	Low	0.04	1.2	0.05	1.5	<0.01	0.12	0.13	3.6
		Median	0.23	6.5	0.41	11	0.04	1.02	0.43	12
		High	1.9	54	4.0	110	0.63	18	3.1	86
Mexico	Mean ingestion	Low	<0.01	0.05	<0.01	0.08	<0.01	0.01	0.04	0.63
		Median	0.01	0.15	0.02	0.31	<0.01	0.03	0.16	2.7
		High	0.18	3.1	0.29	5.1	0.04	0.65	0.47	8.3
	High ingestion	Low	0.01	0.18	0.01	0.30	<0.01	0.03	0.09	2.5
		Median	0.02	0.60	0.04	1.2	<0.01	0.13	0.39	11
		High	0.45	12	0.73	20	0.09	2.6	1.2	33

5.5 Conclusions

- Concentrations of BFRs are on the whole comparable with previous studies, though some differences exist for individual compounds.
- Concentrations of our target BFRs in US dust are at a similar or lower level compared with previous US studies.
- Differences in concentrations of individual BFRs between countries were significant, except for BDE-209 and DBDPE.
- Concentrations of PBDEs (both single congener and total concentration) were the highest in US, and much higher than in all other countries.
- Concentrations of Penta-BDE formulation congeners were found to be the highest in US, followed by Mexico.
- Jordanian samples showed elevated concentrations of Octa-BDE.
- US and Mexican samples showed a similar composition to the FM 550 formulation (EH-TBB:BEH-TEBP 4:1).
- There is no significant difference among countries for concentration of ΣNBFRs.
- For ΣBFRs, US showed a much higher concentration than other countries, followed by Jordan, Spain and Mexico as second group, and then Finland and Greece the lowest.
- Exposures of BDE-47, 99, 153 and 209 via dust ingestion were comparable with previous studies, and far below the reference dose set by US EPA.

Chapter 6 Summary

6.1 Conclusions

This study investigated concentrations of 8 PBDEs, 5 NBFRs and α-, β-, γ-HBCDDs in UK kitchen and living room dust, reporting lower concentrations in kitchen dust than in dust samples from living rooms in the same homes. Untargeted FRs such as TBBPA and PFRs were detected in kitchen appliance surface wipe samples, which can partly explain the lower target BFR concentrations in kitchen dust. Concentrations of PBDEs, DBDPE, and BTBPE in living room dust were compared with 2006-07 UK house dust. A significant decrease in BDE-209 concentrations and a significant increase in DBDPE concentrations were observed since 2006, consistent with restrictions on the use of PBDEs and their substitution by NBFRs.

In total, 96 plastic kitchen utensils were screened using an XRF spectrometer for Br content and 30 of them further analysed for BFR concentrations. Significantly higher Br and BFR concentrations were detected in utensils aged over 5 years than in those younger than 5 years, consistent with the introduction in restrictions in use of PBDEs from the mid-2000s onwards, and the more recent introduction of restrictions on the recycling of BFR-treated plastics. For the BFR distribution patterns in kitchen utensils, BDE-209 was the main BFR in the majority of utensils but the pattern was still very case specific varying from utensil to utensil. Extremely high concentrations of BTBPE,

BDE-153 and BEH-TEBP were observed in some utensils, and the patterns of utensils purchased in the same batch were very similar. Simulated cooking experiments revealed considerable BFR transfer from kitchen utensil to cooking oil, varying between BFR and utensil. Decreasing transfer was observed with the increasing of Br substitution of PBDEs. Using BFR containing utensils for frying may lead to considerable dietary exposure, whilst exposure via dermal contact is less substantial due to limited contact time and the barrier effect of skin.

Significant differences between concentrations of individual BFRs in dust from different countries were observed for almost every single target BFR, except for BDE-209 and DBDPE. Dust from the US displayed the highest overall concentration, followed by Jordan, Spain and Mexico as a second group, with Finland and Greece displaying the lowest concentrations. Moreover, concentrations of Penta-BDE formulation congeners were found highest in dust from the US, followed by dust from Mexico, whilst Jordanian dust showed an elevated concentration of Octa-BDE. There was no significant difference between the studied countries with respect to concentrations of ΣNBFRs, but a similar composition to that observed in the FM 550 formulation (EH-TBB:BEH-TEBP 4:1) was observed in US and Mexican dust.

6.2 Research gaps and future perspectives

This study reported for the first time on BFR contamination in kitchens, reported international variations in the occurrence of NBFRs in dust samples and provided new

data on BFR concentrations in kitchen utensils and the resultant human exposure implications, filling the research gaps to some extent. However, more research is needed in the aspects listed below.

- This study measured BFR concentrations in kitchen dust and transfer from utensils to food during cooking, with concentrations in air and BFR transfer via direct dust/air contact during food storage not measured, which could be an important omission.
- PBDEs, HBCDDs and 5 NBFRs are target compounds in this study, which does not cover the full BFR spectrum. Studies on other BFRs, especially other NBFRs are scarce and thus needed.
- Restrictions on legacy BFRs like PBDEs and HBCDDs have been in place for several years. Systematic studies of time trends in BFR concentrations in various compartment are required to evaluate the impact if such restrictions.
- Applications and restrictions on BFRs may differ by region and country; thus more studies comparing international differences in environmental contamination using identical sampling and analysis methods are needed.

Appendix: Health and Safety Statement

Operation with organic solvent, sulphuric acid, compressed gas is involved in this work, thus risk of inhalation when using solvents, risk of splashing onto skin and into eyes, risk of asphyxiation with N_2, risk of high pressure release of piping and equipment when using compressed gas are concerned. To minimise the risk, researchers should NOT work in the laboratory before attending chemical safety, compressed gas and GC-MS training course, and should follow Good Laboratory Practice (GLP) at any time and work to a suitable and sufficient Hazard and Risk Assessment in accordance with COSHH regulation. Some important H&S statements are listed below.

- Whole procedure to be carried out in fume hood with sash lowered as much as possible.
- Personnel protected by use of laboratory coat, nitrile powder-free gloves and adequate eye protection.
- Solvent and acid disposed in the correct bottle, including hexane and methanol disposed of in non-halogenated waste solvent bottle, dichloromethane waste disposed of in halogenated waste solvent bottle and sulphuric acid waste disposed of in corrosive waste bottle. All waste disposed of as hazardous waste by arrangement with laboratory manager.
- Stand to the side when opening a compressed gas cylinder, always open cylinder valves slowly. Before connecting a regulator, open the cylinder valve slightly and close it immediately.

- Store gas cylinders secured and in an upright position with the cylinder cap on at all times. When transporting cylinders, make sure the valves are closed, remove the regulators, make sure the protection cap is in place and secure the cylinder on a cylinder cart.
- In the case of a large solvent spillage, switch off sources of ignition and close fume hood sash, use personal protective equipment, avoid dust formation, avoid breathing vapours, mist or gas and ensure adequate ventilation. Warn others and retire to safety, contact 1st aid personnel for any affected persons. Absorb spillages onto spillage mats and then place mats into a sealable container and arrange disposal as hazardous waste with the lab manager. Do not let product enter drains.

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